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This is a compilation of papers presented at the first in a series of workshops on environmental monitoring of geothermal energy development held on October 20 and 21, 1975 at the U.S. Environmental Protection Agency's Environmental Monitoring and Support Laboratory in Las Vegas, Nevada. The purpose of this workshop was to generate the exchange of ideas and knowledge needed to develop a set of standard geothermal sampling methods with assurance of quality in those methods. Representatives of industry, universities, and government presented 19 technical papers, 12 of which are published in this document. Their content and the discussions which followed the presentations provided guidance for developing a recognized Referenced Sampling Method Handbook.

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HELD ON
OCTOBER 20-21, 1975

AT THE
ENVIRONMENTAL MONITORING
& SUPPORT LABORATORY
LAS VEGAS, NEVADA

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PROCEEDINGS OF THE FIRST WORKSHOP ON SAMPLING GEOTHERMAL EFFLUENTS

October 20-21, 1975
Las Vegas, Nevada

conducted by

Monitoring Systems Design and Analysis Staff
Monitoring Systems Research & Development Division
Environmental Monitoring and Support Laboratory
Las Vegas, Nevada

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
LAS VEGAS, NEVADA 89114

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FOREWORD

The U.S. Environmental Protection Agency contends that the first step in any viable assessment program is to obtain samples under standard conditions with quality-assured methods. Without this first step, the balance of the examination for pollutants is of questionable value.

In October 1975, the Agency's Environmental Monitoring and Support Laboratory in Las Vegas held an initial workshop on geothermal energy development. The purpose of this first workshop was to generate that necessary exchange of ideas and knowledge needed in developing a set of standard geothermal sampling methods with assurance of quality in the methods. The goal of this effort was the formation of a recognized Standard Sampling Method Handbook. The response to this first workshop was encouraging, leading us to strongly believe that the goal is attainable.

The Environmental Monitoring and Support Laboratory-Las Vegas wishes to take this opportunity to express its appreciation and gratitude to those organizations and persons who gave so freely of their time and resources to make this first meeting a success.

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GEOTHERMAL ENERGY DEVELOPMENT*

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*based on reports prepared during Leave of Absence 1974-75 with the National Science Foundation and the Energy Research and Development Administration.

INTRODUCTION

The Nation has embarked on an aggressive program to develop its indigenous resources of geothermal energy. For more than a decade, geothermal energy has been heralded as one of the more promising forms of energy alternate to oil and gas for electric power generation, but during the last fifteen years, the total capacity in the U.S. has reached 502 MWe, about half the size of a single modern nuclear power plant. And yet, the United States, especially its western and Gulf coast states, is believed to possess a vast resource base of geothermal heat at depths up to 3 to 10 km. Many estimates of these potential resources suitable for the production of electric power have been published and they range over a spectrum of more than a factor of 100. This variation suggests that the potential is essentially unknown.

Table 1 gives a range of published forecasts for the year 1985 and the equivalent potential in number of 1000 MWe power plants and in oil consumption in millions of barrels per day. In view of the estimated construction of about 200 to 250 nuclear power reactors by 1985-90, the pessimistic forecasts clearly show that the contribution of geothermal energy to the Nation's energy supply may indeed be small. The optimistic forecasts represent more than 15% of the total electric power requirements estimated for the year 1985. The Task Force for Geothermal Energy, in the Federal Energy Aministration Project Independence Blueprint report of November 1974, established a national goal for 1985 of 20,000 to 30,000 MWe, the latter value representing an equivalent energy supply of one million barrels of oil per day. This goal was

TABLE 1

FORECASTS AND NATIONAL GOAL FOR DEVELOPMENT OF U.S. GEOTHERMAL RESOURCES

	PESSIMISTIC FORECASTS	NATIONAL GOAL 1985	OPTIMISTIC FORECASTS
ELECTRIC AND THERMAL ENERGY CAPACITY (MW)	2000 - 4000	20,000 - 30,000	182,000 - 400,000
EQUIVALENT IN NUCLEAR REACTORS (NO. 1000 MWE UNITS)	2 - 4	20 - 30	182 - 400
EQUIVALENT CONSUMPTION OF OIL (10^6 BBL/DAY)	0.07 - 0.14	0.7 - 1	6 - 14

clearly a compromise between what is worth a national effort and what might be realistically achieved. The potential for adding or replacing the equivalent of some 25 nuclear power plants or for conserving one million barrels of oil per day should be an adequate incentive for the Nation to accelerate the development of a viable geothermal industry.

A puzzling enigma appears. If the potential resource base of geothermal energy is so vast, why has significant utilization not occurred? The entire U.S. production of electric power from geothermal resources occurs at one location, the Geysers in California, where over a 15-year period starting in 1960, generating capacity has grown from 12 MW supplied by Unit No. 1 to the total of 502 MW attained with the startup of the 106-MW Unit No. 11 in May 1975. The Geysers is the largest geothermal electricity generating station in the world. The entire worldwide capacity of electric power generation by geothermal resources is slightly more than 1000 MW, the equivalent of the capacity of a single modern nuclear power plant.

Utilization of geothermal fluids for thermal energy in the U.S. is almost negligible. And yet throughout the country, fossil fuels are consumed in large quantities to boil water for heating and electric power generation, both at very low thermal efficiency. Some countries already use geothermal fluids for its thermal energy, notably Iceland, where municipal heating is an important utilization. Several countries, responding to increased public awareness that future supply of fossil fuel may be very limited, are examining the potential use of indigenous thermal waters for industrial and municipal heating.

How is this enigma to be solved; how is the United States (and other countries) endowed with potentially-bountiful geothermal resources going to develop these natural resources as a significant contribution to its energy supply? The attainment of a national goal to contribute an equivalent of one million barrels of oil per day from geothermal resources clearly requires accelerated development of a geothermal industry capable of providing 20,000 to 30,000 MW of electric power and thermal energy in the next ten to fifteen years. And this objective will require a national effort to accelerate and coordinate development in three parallel tasks: (1) the discovery, proving, and extraction of geothermal resources to provide a significant supply of hydrothermal fluids for direct utilization and to produce more than 5×10^{12} kWh of electricity over the amortization period of the investment in resource development and power plant construction, (2) the technology to convert the resources as found in its various natural forms and qualities into electricity, and (3) the removal of unnecessary institutional constraints to the rapid development of a cost-effective and environmentally-acceptable industry.

A major factor which helps create the enigma of vast resource base and little utilization is the variability of geothermal resources. The geothermal energy cycle, although simple compared to other alternate energy sources, is actually complex in that geothermal resources occur in many types of geologic, thermodynamic, hydrodynamic, and chemical quality. As a result, the major problems in the energy cycle vary by type of resource. Table 2 lists the key aspects of the cycle from exploration to utilization that must be evaluated for each type of resource.

Several general reviews of the state of the art of geothermal energy resources and technology are listed in the Bibliography. One is

TABLE 2

PROBLEM AREAS IN THE DEVELOPMENT OF THE GEOTHERMAL ENERGY CYCLE

VARIABILITY OF GEOTHERMAL RESOURCES
LOCATION OF SUBSURFACE RESERVOIRS
RESERVOIR EVALUATION
EXTRACTION TECHNOLOGY
CONVERSION TECHNOLOGY
POTENTIAL FOR MULTIPLE UTILIZATION
ENVIRONMENTAL IMPACT CONTROL
LEGAL AND INSTITUTIONAL CONSTRAINTS

the proceedings of the 1970 United Nations symposium on the development and utilization of geothermal resources. Another is the 1973 compilation of an Ad Hoc Working Group convened by UNESCO. A general introduction to geothermal energy is the proceedings of the American Nuclear Society conference on geothermal resources, production, and stimulation held in 1972. Among other compilations of papers on geothermal energy are the proceedings of the second and third All-Union conferences on geothermal energy organized by the Scientific Council for Geothermal Investigations of the USSR Academy of Sciences. Translations of these proceedings are not generally available, but much of the technical content is given in the Soviet papers of volume 2 of the United Nations Symposium and in the ARPA reviews of Soviet literature in geothermal energy. The proceedings of the Second United Nations Symposium held in San Francisco in May 1975, adds another major contribution to the literature of geothermal energy.

GEOTHERMAL RESOURCES

The upper 10 km of the earth's crust may contain more than 3×10^{26} cal of heat, a resource base readily classified as vast. However, much of this energy is too diffuse to be exploitable as an energy source. Geothermal resources may be defined as localized deposits of geothermal heat concentrated at attainable depths, in adequate volumes, and at temperatures sufficient for commercial exploitation.

The only geothermal resources presently used for electric power generation are high-quality hydrothermal convective systems which contain high-enthalpy geofluids suitable for transferring the geothermal heat to the surface for direct use in low-efficiency steam turbines.

Unfortunately such resources have been discovered at only a few places on earth. More than 75% of the world's geothermal electric power capacity results from vapor-dominated hydrothermal systems which produce dry or super-heated steam for direct conversion. The remaining capacity results from high-temperature, low-salinity, water-dominated hydrothermal systems in which the geofluids are flashed on production, and only the seperated steam is used for electric power generation. The liquid fraction is either wasted or reinjected into the ground. These systems are commercially less desirable because only a small fraction of the water flashes to steam, thermal efficiencies are low, and plant operational problems are more severe.

Liquid dominated hydrothermal systems are expected to be many times more abundant than vapor-dominated hydrothermal systems. Moderate-to-high salinity hydrothermal resources may be more abundant than low salinity resources. And other types of geothermal resources, such as hypersaline brines, geopressured fluids, volcanic and magmatic deposits, and impermeable hot-rock massives, which are not yet commercially exploitable, may be even more abundant than the currently exploited hydrothermal resources. Thus the answer to the utilization enigma may lie not so much with the magnitude of the resource base, but more with the ability to locate suitable concentrated deposits of geothermal heat and the technology to extract the energy in quantities which are economically and environmentally feasible.

Although estimates of the geothermal resource base are available, the magnitude of the potential reserves is not yet well defined. The location of underground deposits of geothermal heat, especially where thermal manifestations are not visible at the surface, is a difficult task. Over one million acres of "hot spots," areas of known geothermal energy, were identified as early as 1967 by the U.S. Department of the Interior in designated Federal lands in five western states as having current potential value as geothermal resources. An additional 86 million acres of land in thirteen states were designated as prospectively valuable for geothermal resources. Since then several other inventories of known geothermal resource areas (KGRA) have been compiled. A current assessment of U.S. geothermal resources has been completed by the U.S, Geological Survey and a summary of the resource base, by resource type, is given in Table 3.

Exploration for geothermal resources has been undertaken by industry on private lands, and through the Federal Leasing Act of 1970, on Federal lands by competitive and non-competitive leasing under supervision of the Bureau of Land Management. Although total values are difficult to ascertain, it is estimated that about 100,000 acres on Federal public lands and about 200,000 acres on Federal Indian lands were under lease for geothermal exploration in mid-1975.

Resource exploration and assessment of potential reservoirs of geothermal energy are made by the variety of earth science methods listed in Table 4. Details of these methods are available in the general references listed in the Introduction. The final phase of geothermal exploration is the drilling of exploratory wells. It is from these wells that data for evaluating the suitability of the resource as a production reservoir are obtained. Major factors in the economics of exploration and production of geothermal fields are the success of

TABLE 3

SUMMARY OF GEOTHERMAL RESOURCE BASE OF THE UNITED STATES*

	Estimated Heat Content (10^{18} cal)	
	Identified	Potential
Hydrothermal convection systems		
Vapor-dominated (steam)	26	50
High T - hot water (T > 150°C)	370	1,600
Mod T - hot water (90° - 150°C)	345	1,400
Total	740	3,000
Hot igneous systems		
Magma and hot rock	25,000	100,000
Geopressured basin part of regional conductive systems	10,920	44,000
Total Resource Base	36,660	147,000

*From D. F. White and D. L. Williams, eds., Assessment of Geothermal Resources of the United States - 1975, U. S. Geological Survey Circular 726, 1975.

TABLE 4

GEOTHERMAL EXPLORATION METHODS

- EXPLORATION SURVEYS
    - AIRBORNE
        - AEROMAGNETIC SURVEY
        - THERMAL INFRARED SURVEY
    - GEOLOGICAL
        - TECTONICS AND STRATIGRAPHY
        - RECENT FAULTING
        - DISTRIBUTION AND AGE OF VOLCANIC ROCKS
        - THERMAL MANIFESTATIONS
    - HYDROLOGIC
        - SURFACE DISCHARGE OF GEOFLUIDS
        - TEMPERATURE OF FLUIDS
        - CHEMICAL COMPOSITION OF FLUIDS
        - GROUNDWATER HYDROLOGY
        - METEOROLOGY
    - GEOCHEMICAL
        - CHLORIDE CONCENTRATION
        - SiO_2 CONTENT
        - NA-K-CA RATIOS
        - ISOTOPIC COMPOSITION OF HYDROGEN AND OXYGEN
    - GEOPHYSICAL
        - GEOTHERMAL GRADIENT
        - HEAT FLOW
        - ELECTRICAL CONDUCTIVITY
        - SEISMIC ACTIVITY
- EXPLORATION HOLE DRILLING
    - RESERVOIR CHARACTERISTICS
        - TEMPERATURE-DEPTH PROFILE
        - PRESSURE-DEPTH PROFILE
        - LITHOLOGY AND STRATIGRAPHY
        - PERMEABILITY LOG
        - POROSITY LOG
        - FLUID COMPOSITION

techniques available for surface exploration of potential resources and exploratory drilling of potential reservoirs. Improvements and novel methods for reducing costs in these two initial phases of the geothermal energy cycle are thus of great importance. In order to achieve the goal of providing an equivalent of one million barrels of oil per day by geothermal resources, it is evident that exploration for geothermal resources, especially hydrothermal, must receive a very high priority by the U.S. energy resource industry.

The magnitude of hydrothermal resources required can be estimated from the following calculation for a 100 MWe generating plant operating with flashed steam of 555 kcal/kg (1000 Btu/lb) heat content. The required geofluid production rate for a hot-water system yielding 10% steam on flashing with a thermal efficiency of 20 percent, would be 7.75×10^6 kg/h (1.7×10^7 lb/hr). The amortization of the 100 MWe plant over a period of thirty years would require a total production of 2.1×10^{12} kg hot water, and a mean reservoir porosity of 10 percent would require a geothermal reservoir volume of about 2 km^3. At a 50 percent condensation efficiency, the plant would discharge a hot water supply of about 100,000 m^3/d (2.5×10^7 gpd).

For a national capacity of 20,000 MWe, these values are multiplied by a factor of 200. Thus reservoirs supporting 200 units of 100 MWe generating plants must be located. These reservoirs will produce about 1.5×10^9 kg/h of hot water. For a mean well production flow rate of 250,000 kg/h a total of 6,000 production wells will be needed, and for a mean spacing of 100,000 m^2/well (25 acres/well), a total reservoir area of 6×10^8 m^2 (1.5×10^5 acres) of geothermal resources must be found. It is evident that if hydrothermal systems are to provide the nation with 20,000 MWe, very high priority for resource exploration and assessment is indeed required.

UTILIZATION TECHNOLOGY

Utilization of geothermal energy varies with the quality of available resources. It has been noted that the present geothermal industry has focused on high quality hydrothermal resources. Extraction and conversion technologies for dry-steam reservoirs are sufficiently advanced to be commercially attractive. Conversion technologies for hot-water resources are more complex, and for hot brines, geopressured basins, and hot dry rock formations, they are even more complex; commercial utilization is still further away. Since these latter types of resource hold great promise, technology to exploit them must be developed.

Stimulation of geothermal energy production can be achieved by research and development to (1) increase the modes of resource utilization, (2) improve energy conversion technology, and (3) provide advanced methods of energy extraction. Increased efficiency in each of these three aspects of the geothermal energy cycle is attainable.

Development of a geothermal field generally involves the geofluid characteristics, steam separation and gathering facilities, turbine and generator equipment, cooling systems, and condensate disposal methods. Such development presupposes that electric power generation is the sole purpose of the field development. It may turn out, however, that for many geothermal reservoirs, non-electric utilization of the resource may make the reservoir economically feasible, with significant conservation of fossil and nuclear fuels. Several modes of utilization of geothermal resources are listed in Table 5. Hydrothermal fluids with temperature or enthalpy too low for economic electric power production may be useful for water or mineral sources and for industrial, agricultural, and municipal heating. However, since major interest in geothermal energy is for the production of electric power, combined or total utilization may help make many geothermal reservoirs submarginal in power production alone become economically feasible. The possibility of building a community around a geothermal resource, with municipal heating, an industrial park of process firms requiring hot water and concomitant electric power production appears feasible. Thus, research for methods stimulating geothermal resource utilization in all forms is well warranted.

General methods for producing electricity from geothermal fluids are summarized in Table 6 and are described adequately in the several cited references. The choice of a conversion cycle is generally dependent on the thermodynamic and chemical properties of the geofluid. Present commercial plants utilize low-salinity hydrothermal systems with steam or water at temperatures above about 200°C in the single-stage direct steam turbine conversion system. To utilize lower temperature fluids, investigations are underway to develop other conversion systems; among these are multiple-flash low-pressure steam turbines, single and multiple stage binary cycle systems, and hybrid systems combining these two. The binary system appears to be the most promising for utilization of geofluids with temperatures between 100°C and 200°C. However only one experimental facility, the Pauzhetka station in the Kamchatka peninsula of the USSR, has been constructed to date. The binary system most likely to be successful in the U.S. will require a downhole pump to prevent flashing, a heat exchanger which can operate without excessive

Table 5

UTILIZATION OF GEOTHERMAL ENERGY

Electric Power Production

- Direct use of dry steam
- Flashing of hot water to steam
    - Surface flashing
    - In-situ flashing
- Binary and hybrid cycles
- Innovative single-well converters

Direct Use of Thermal Waters

- Agriculture
- Aquiculture
- Space heating
- Industrial processing
- Medical therapy

Byproducts

- Mineral extraction
- Water resources

TABLE 6

TYPES OF GEOTHERMAL POWER PLANTS

HEAT SOURCE	GENERATION MODE
DRY STEAM	STEAM TURBINE
HOT WATER (T > 180°C)	STEAM TURBINE
HOT WATER (T < 150°C)	BINARY CYCLE
HOT WATER (MODERATE SALINITY)	HYBRID CYCLE
HOT BRINE (PRESSURIZED)	BINARY CYCLE
HOT BRINE (FLASHED)	IMPACT TURBINE HELICAL SCREW EXPANDER BLADELESS TURBINE

corrosion and deposition, and a circulation system which allows for reinjection of the geofluids for environmental control purposes.

Several types of downhole pumps are under development, involving design concepts which use (a) in-situ heat to operate a closed steam-generator-turbine to drive the pump, (b) a high-speed, high-temperature high length-to-diameter electric-motor driven pump, or (c) a hydraulically driven unit with hydraulic power from the surface. Heat exchanger concepts include fluidized sand beds to enhance heat transfer rate and maintain clean surface, and liquid-liquid systems with direct contact of immiscible fluids, tray-tower contactors, or subcritical or supercritical power cycles.

Flash and binary systems are useful in large power plants having capacity in excess of 50 MWe. They require complexes of multiple-well field development and extensive networks of gathering lines. Innovative conversion systems are under development in which small power plants, in sizes of 1 to 15 MWe, may be installed at individual wells. These systems may involve a total flow concept in which both the thermal and kinetic energy of the geofluid is used for production of electricity.

One of these is the impulse turbine, in which the thermal energy is converted to kinetic energy through a converging-diverging nozzle, and the high-velocity output drives a hydraulic impulse turbine operated at low pack pressure. Calculations indicate that a large unit (e.g., 220 MWe) might be feasible for the Salton Sea geothermal brines, which contain as much as 230,000 ppm total dissolved solids. The material handling problems of such brines are indeed enormous, but the dissolved solids may also represent a source of valuable minerals, such as lead, manganese, and copper, if they can be processed economically.

Another total-flow concept is the helical rotary screw expander which expands the vapor from hot saturated liquids by continuous pressure reduction in the expanding screw, in essence creating an infinite series of flashing stages. A small 62.5 kV prototype model was tested successfully with moderate salinity geofluids with indications that it can accept the total flow of untreated brines. Still another concept is the bladeless turbine, in which a series of closely-spaced disks are rotated by viscous drag exerted by geofluids introduced by a nozzle. The device seems simple and self-cleaning, but the overall efficiency may be small.

Increased extraction efficiency represents a major means to stimulate geothermal energy production, especially for non-hydrothermal reservoir systems. Calculations show that hot-water reservoirs contain a larger amount of available energy than steam-filled reservoirs under the same reservoir conditions because of the much larger mass of water; but in either system, the heat contained in the rock formation is much larger than the heat in the fluids. Thus recovery of the formation heat would be of major economic significance. Extraction of formation heat must be a non-isothermal process, which can be achieved either by flashing geothermal liquids to steam within the formation or by recycling colder fluids back into the formation. Laboratory investigations and theoretical calculations of reservoir models are underway to determine the extent of heat extraction from fractured reservoir formations.

The natural extraction efficiency of energy from impermeable hot dry rock formations is extremely small. And yet hot dry rock in the upper 10 km of the earth's crust represents a major potential resource of geothermal energy. The volumetric energy extractable from hot dry rock, calculated for average expected properties and possible technical extraction efficients, is of the order of 1.2 x 10^9 kWh/km^3 of fractured rock, equivalent to a volumetric power extraction of 1.4 MW/km^3 for one century. The technical challenge is the ability to fracture such volumes of hot rock massives and achieve an extraction efficiency of the order of 10 percent.

Fracture stimulation methods are useful for many types of geothermal reservoirs. In vapor-dominated systems, stimulation may restore declining pressure or connect dry holes in commercial steam fields to producing sections. In liquid-dominated systems lacking sufficient productivity for economic power generation, fracture stimulation may provide larger wellbore diameter for increased flow rate, greater surface area for heat transfer, or restore porosity or permeability around wells having deposited silica, calcite, or other precipitated minerals. In dry geothermal systems, stimulation is needed to provide large fracture volumes for heat transfer to an artificial convective extraction system.

Several fracturing methods are under study; these include hydraulic fracturing, thermal stressing, and chemical and nuclear explosive fracturing. Hydraulic and explosive fracturing methods have already proven successful in stimulation of natural gas reservoirs.

Experiments to evaluate the potential for hydraulic and thermal stress fracturing for recovery of geothermal energy from hot dry rock formations are underway. In this concept a large diameter vertical crack is created hydraulically at the bottom of a boreholde in the geothermal formation. A second hole is drilled to intersect the upper part of the fracture, and a pump is used to initiate artificial heat-extraction circulation. It is hoped that pumping can be discontinued if a natural convective circulation is achieved. The major technical problems are the attainment of a vertical crack of about 2 km diameter with sufficient fracture area, the creation of additional fracture area by thermal stress of cold water injection, and the ability to achieve a natural convective circulation without undue losses of water, especially in arid regions. Calculations indicate that under favorable conditions, the system might provide an average power of about 100 MW (thermal) for twenty years.

INSTITUTIONAL ASPECTS

Although much remains to be done in locating adequate reserves and developing adequate technology to meet the goals for exploiting the Nation's geothermal resources, there is great confidence that these will be achieved. These problems involve advances in physical research and technology. Institutional problems however, also exist. Such problems are complex; they involve public acceptance, vested interests, historical precedents, existing regulations from other resources, overlapping jurisdictions, and economic and financial factors. These problems are often more difficult to resolve than are engineering problems, and they may in the long run be the major constraints to an accelerated, but orderly development of geothermal resources. The solutions to many institutional problems may require broad public interaction, changes in regulations and legislation, and perhaps changes in traditional investment and marketing procedures.

Economic factors affect all forms of energy supply; they involve total capital costs per installed power unit and operational costs per unit of energy production. For geothermal energy, both of these cost factors are strongly dependent on the specific characteristics of individual reservoirs and the size of the installed power plant units. Important capital costs include the investments for exploration, drilling and completion of wells, gathering lines and waste handling systems for all utilizations. For thermal energy applications, they also include the distribution system, and for electric power production, they include the power plants and the transmission network. The production costs are influenced by the cost of capital, operations and maintenance, and plant utilization factor. In the United States, additional costs must also be added for environmental pollution control.

Factual cost data for geothermal electric power production in the United States are available only for the Geysers field. The electric utility purchases steam from only one supplier, but has negotiated to purchase steam for future plants from additional suppliers. In the development of future geothermal power stations, an option exists for an integrated operation from exploration to power production in contrast to the traditional roles of an electric utility purchasing steam or hot water from an independent supplier. The general effect would be an increased investment cost per kilowatt hour of energy.

Data for costs of recently-constructed power plant units at the Geysers are sparse, but estimates for the original plants range from about $100 to $150 per kW. Production costs were estimated at about 7 mill/kWh of which about 3.5 mill/kWh was the price of the purchased steam. These estimates included a cost of 0.5 mill/kWh for injection of water condensate as a disposal method. With escalation of drilling, construction, and environmental reporting costs over the past few years, these cost values are not useful for estimating costs of new facilities, especially for reservoirs which do not produce dry steam. Recent estimates indicate installation costs may range from $500 to $700 per kW and operating costs for binary conversion systems of the order of 20 to 40 mill/kWh. These costs, of course, are hypothetical, and more precise costs will be generated as other major reservoirs and plants are developed and operated. A large uncertainty in the total cost is the fixed exploration cost for the resource, which is independent of plant capacity, and the average drilling costs of the production, dry, and injection wells. Computer models to evaluate the relative importance of these resource and utilization costs are under development.

Because of large uncertainties in the technical costs of exploration and drilling, conversion efficients, and stimulation techniques, and because of the rapid escalation rate of these costs, it is difficult not only to estimate costs on an absolute basis, but even to compare costs of other forms of electric power generation. Besides the costs affected by these technical factors, other factors more social in nature must be considered. Among these are public acceptance and government stimulus for accelerating the development of geothermal energy in relation to other energy sources, the interpretation of compliance with the National Environmental Protection Act of 1969, and the availability of investment capital for development of geothermal resources and electric and thermal power plants. These socio-economic factors may require much public and government deliberation before general philosophies are widely accepted in practice.

Although geothermal energy is considered to be one of the least polluting of the many forms of energy available, it should be assumed that the public will insist that the environmental impact of producing geothermal energy in all of its natural and stimulated forms, be thoroughly investigated in accordance with NEPA and any additional requirements under state and local legislation. Furthermore, in addition to environmental impact, it is also evident that assessment will be required of the operational aspects of the various types of resources which affect personnel safety and plant maintenance.

In the evaluation of a benefit-risk analysis, geothermal energy is expected to compare favorably with respect to other energy resources, especially when viewed over the entire fuel cycle. Since geothermal energy must be utilized or converted in the vicinity of the resource, the entire "fuel cycle" from reservoir to transmission is located at one site. This is in contrast with material fuels in which the cycle involves mining, storage, refining, transportation, reprocessing, and waste disposal, many or all of these at different locations. Furthermore, increased utilization of geothermal energy may result in a correspondingly reduced demand for material fuels in short supply, such as natural gas, oil, coal, and uranium. And still further, geothermal fluids may provide byproduct sources of water with reduced demand for cooling water.

Geothermal energy, nevertheless, has its array of potentially deleterious environmental impacts. A list of potential environmental impacts is given in Table 7. A review of the more important ones has recently been completed in a workshop sponsored by the National Science

Table 7

Environmental Impacts of Geothermal Power Production

Land	Water	Air
Land Utilization ~2 km^2/100 Mw	Disposal of Drilling Fluids	Release of Steam and Other Gases during Drilling and Testing
Drilling Operations ~20 Wells/km^2	Need for Supplementary Cooling Water	Noise Pollution
Power Plant Construction 1 plant/100 Mw	Build-up of Salt Concentrations	Release of H_2S and Other Non-condensable Gases
Steam Gathering Lines ~0.2 km/100 Mw	Disposal of Condensor Cooling Water Steam Condensate ~3.5 Mgpd/100 Mw	Potential Changes in Micrometeorology
Condensate Reinjection Lines and Pumps	Potential Mineral and Thermal Pollution of Fresh Surface Waters	Potential for Well Blowout
Potential for Land Subsidence Seismic Activity		

Foundation (see [7] in Bibliography) as the basis for a program to support research for baseline data and technology for monitoring potential impacts and controlling actual hazards. The major impacts include gaseous emissions, liquid waste disposal, and geophysical effects such as seismicity and subsidence. Other concerns involve thermal releases, surface water contamination, land use planning, cooling water consumption, and visual and noise pollution.

An array of legal problems associated with geothermal resource development also exists. These have been reviewed in another workshop sponsored by the National Science Foundation (see [8] in Bibliography).

The legal problems of geothermal resources begin with resource definition, which varies from state to state. For example, in California geothermal resources are defined as "the natural heat of the earth, the energy--which may be extracted from naturally heated fluids--but excluding oil, hydrocarbon gas or other hydrocarbon substances." This definition leaves open the question whether geothermal resources are legally defined as water, mineral, or gas resources, and results in large uncertainty with respect to Federal, state, and local jurisdictions. On the other hand, the State of Hawaii considers geothermal resources as minerals, whereas the State of Wyoming has declared them water resources. As water resources, they would be subject to the very complicated set of state laws concerning water rights and regulation. As minerals, they would be subject to mining laws and such problems as ownership, depletion allowances, and write-off of intangible drilling costs. Geothermal resources have already been classified in court decisions in different ways. In one case a U.S. District Court in San Francisco treated the

Geysers geothermal resource as "nothing more than superheated water" and therefore not a mineral, but in another case, the resource was held to be a gas within the meaning of the Internal Revenue Code provisions for depletion allowance and intangible drilling costs.

Ownership rights is also a serious institutional problem. The Federal government has given some 35 million acres of land to the homesteaders, States, and railroads, but generally reserved the mineral rights to the Federal government. However some State grants included mineral rights and thus many problems exist in the ownership aspects of Federal and State lands under the leasing of these lands for geothermal energy development. Land utilization for geothermal resources also comes under the jurisdiction of local governments, except for resources on State or Federal lands.

Other institutional questions at the State level include the acreage level for commercial development, the need for long-range financial and land use planning, and the overlapping of State regulatory agencies with each other and with jurisdictions of local governments for permits, licences, taxation, and especially environmental control. The latter may be affected at the Federal, State, regional, county, or city government levels. For example, in some areas, authority may be divided between such agencies as a Regional Land Development Commission and a County Air Pollution Control Board.

The institutional aspects of licensing and regulation of power plants is very complicated; they cover the spectrum from Federal to local jurisdictions. Regulations already exist with respect to the exploration, drilling and operation of water and mineral wells in all states. The extension to geothermal wells should be relatively simple. Yet the need to satisfy the provisions of NEPA and any specific State environmental requirements may make geothermal resource development a slow process. For example, in California, the State Lands Commission, before it can lease any lands under its jurisdictions, must make a finding at a public meeting that the lease will not have significant detrimental environmental effect and must prepare an environmental impact report available to the legislature and the public. The corresponding problems of environmental impact from geothermal resources in private lands are not yet fully resolved.

Once the field is developed to the point where a utility contracts to purchase the resource and construct a power plant, other regulatory agencies come into the picture, such as the Federal Power Commission and corresponding state and local agencies. Site selection and environmental analysis criteria are becoming of major importance in power plant licensing for all types of energy resources and their effect on geothermal energy development will probably be determined by solution of these problems on a generic basis, rather than specifically for geothermal energy alone.

Institutional problems thus involve many social, legal, environmental, and economic questions. The problems become more complex for land use planning when geothermal resources span Federal, state, and private lands. They involve capital investment problems for geothermal development which may be considered to be high-risk and involve long-delay times until they become income producing. They involve inter-industry arrangements when multi or total utilization is needed to support economic development of electric power generation, thermal power heating, desalination and mineral recovery. And they involve multi-government arrangements in the realms of regulation, licensing, and environmental control.

NATIONAL GEOTHERMAL PROGRAM

Although significant growth of the one natural steam field in the United States has occurred since 1960, it has become apparent that a major national effort of industrial development supported by Federal stimulation is needed to develop the potential of geothermal resources in its several forms as an alternate energy source. Early efforts to achieve a coordinated Federal program for the support of research and development were undertaken by an informal Interagency Panel for Geothermal Energy Research. From these efforts evolved a 5-year program whose objective was the rapid development of a viable geothermal industry for the utilization of geothermal resources for electric power production and other products. The goals and plans for this program were prepared by the Interagency Task Force on Geothermal Energy under direction of the National Science Foundation in the Federal Energy Administration "Project Independence Blueprint" (see [9] in Bibliography). The task force evaluated two alternate strategies. The first was "business-as-usual" which assumed continuation of current policies affecting levels of geothermal production. The second was "accelerated demand" which assumed specific changes that would result in a more rapid expansion of potential production.

The task force estimated that under the "business-as-usual" assumptions, electric power capacity could reach 4000 MWe by 1985 and perhaps 59,000 MWe by 1990. The corresponding numbers for the "accelerated demand" assumptions were 20,000 to 30,000 MWe by 1985 and 100,000 MWe by 1990. These latter values were adopted as the primary goal of a proposed National Geothermal Energy Research Program, which was directed towards (1) providing the necessary technological advances to improve the economics of geothermal power production, (2) expanding the knowledge of recoverable resources of geothermal energy, and (3) providing carefully researched policy options to assist in resolving environmental, legal, and institutional problems.

The major research funding agencies which contributed to the task force program were the Atomic Energy Commission, the Department of the Interior, and the National Science Foundation which served as lead Federal Agency. The status of the research carried out under support from these agencies is described in the proceedings of a conference on research for the development of geothermal energy resources (see [10] in Bibliography).

During 1974, two acts of Congress resulted in a marked change in direction for the national development of geothermal energy. The first was PL 93-410, the Geothermal Energy Research, Development, and Demonstration Act of 1974, which established a Geothermal Energy Coordination and Management Project. The Project was given responsibility for the management and coordination of a national geothermal development program which included efforts to: (1) determine and evaluate the geothermal resources of the United States; (2) support the necessary research and development for exploration, extraction, and utilization technologies; (3) provide demonstration of appropriate technologies; and (4) organize and implement the loan guarantee program authorized in Title II of the Act.

The second law was PL 93-438, the Energy Reorganization Act of 1974, which established the Energy Research and Development Administration, ERDA, with responsibility as lead Federal agency for activities related to R&D of all energy sources. The Act abolished the AEC and transferred the geothermal development function of the AEC and NSF to ERDA. On January 19, 1975, ERDA assumed responsibility for the national program of geothermal energy development. It has also assumed direction of the Geothermal Energy Coordination and Management Project which has completed the Final Report required by PL 93-410 (see [11]). In addition, ERDA, in response to Congressional requirements and internal needs, prepared a comprehensive R,D&D plan (see [12]) for developing energy technology options. The geothermal section of the plan built upon the predecessor plans of the Task Force for Geothermal Energy and the Geothermal Project and has based the goal for the national program on the rational given in Volume 2 of the Plan.

The objectives being considered in the ERDA program for geothermal energy include methods to stimulate the industrial development of indigenous hydrothermal resources to provide the Nation with 10,000 to 15,000 MW of electric power and thermal energy during the 1985 to 1990 period and to develop new and improved technologies for cost-effective and environmentally-acceptable utilization of all types of geothermal resources as a long-term alternate source of energy.

The strategy of the program which might accomplish such objectives would be to accelerate industrial development of the nation's geothermal resources by (1) coordinating efforts for exploration and assessment of geothermal resources necessary to establish reserves by 1978-1980 which can support production of 20,000 to 30,000 MW of power,

(2) demonstrating near-term and advanced technologies needed to utilize many types of geothermal resources in a cost-effective and environmentally-acceptable manner, and (3) fostering rapid development of a viable geothermal industry by appropriate incentives, timely reduction of institutional impediments, and direct participation of the private sector in development and demonstration of geothermal energy technology.

Although ERDA assumes overall responsibility for effective management and coordination of Federal geothermal activities, the scope of the Federal program includes the efforts of many Federal agencies. The Geothermal Steam Act of 1970 authorized the Department of the Interior to lease Federal lands for geothermal resource exploration, development, and production of energy and useful byproducts (such as methane, desalinated water, and valuable minerals). The leasing program is conducted by the Bureau of Land Management which is responsible for selecting lands for lease and holding lease sales and the U.S. Geological Survey which classifies the lands by appraised value.

The U.S. Geological Survey's geothermal research program is focused on the characterization and description of the nature and extent of the geothermal resources of the United States. The output of the U.S. Geological Survey's program is the determination of the magnitude of the geothermal resource base on a national and regional basis. The Survey's program includes development of exploration technology, methodology for estimating energy potential of geothermal systems, environmental effects of geofluid withdrawal, and geochemical aspects of reservoir permeability.

Some of the problems that have retarded the delineation of the Nation's geothermal resources through the leasing of public lands include the lack of reliable information regarding suitable resources, even on lands classified as KGRAs, insufficient requirements for early exploration and development of leased lands, and legal problems involving ownership and control of use of geothermal resources. Under a national program, coordinated effort by ERDA and the Department of the Interior would help to accelerate the establishment of geothermal reserves by the resource industries. Potential actions include (1) accelerated estimation by the U.S. Geological Survey of the available resources by geologic type, (2) improved technology for resource exploration and assessment and for reservoir evaluation, (3) easing of leasing impediments by better methods for designating KGRAs and establishing minimum acceptable bids, (4) incentives for early development of leased lands, and (5) recommendations for legislation to resolve legal uncertainties pertaining to geothermal resources.

The second part of the strategy for the Federal program would center on ERDA efforts for demonstration of near-term and advanced systems for resource utilization, development of supporting research and technology, and execution of the Federal loan guarantee program. Demonstrations of utilization technology could occur as (1) commercial-scale demonstration plants to provide the public sector with operational experience with full-scale electric power plants capable of generating energy at design production cost under pertinent environmental and institutional conditions, (2) pilot-plant facilities to prove technical feasibility, provide preliminary economic data, and provide capability for testing new and improved extraction and conversion systems for electric power production, and (3) field test facilities to improve reservoir assessment technology, evaluate reservoir characteristics and performance, test and evaluate energy extraction and conversion components and processes, evaluate material compatibility with geothermal fluids, and test environmental control technologies. A supporting research and development program could provide for development of hardware systems, components, processes, and control techniques for installation in the demonstration facilities and field testing of reservoir evaluation technologies for the range of resource types. Supporting research and development program could also provide advanced research and technology to the geothermal industry and its supplier and support industries for improved productivity and utilization.

Implementation of the Loan Guarantee program should be coordinated with the Bureau of Land Management's geothermal leasing program and ERDA's research, development, and demonstration program. The program could involve venture capital companies, reservoir developers, and lease holders to maximize the impact of the loan program in stimulating early development of commercial electric and thermal power facilities. The Loan Guarantee program might be used primarily for income-producing projects, such as field development and power-plant construction. Smaller industrial firms could benefit from guaranteed loans by gaining access to necessary private capital. Regulations and procedures governing the implementation of the loan guarantee program are currently being drafted in coordination with other Federal agencies, such as the Small Business Administration and the Economic Development Administration. Approved regulations and operating procedures setting forth specific information requirements to be met by the applicant and criteria governing the approval process should be widely publicized as early as possible.

The third part of the strategy of the Federal program would involve several Federal agencies, notably the National Science Foundation, involved in assessing environmental, legal, and institutional problems of advanced energy technology under its RANN program, the Environmental Protection Agency, involved in environmental emission standards, monitoring, and control technologies, and the Federal Energy Administration, involved in institutional aspects of the national energy situation.

With the mutual efforts of the Federal program and the geothermal industry, the attainment of the National electric and thermal energy goals for geothermal resources could add a significant alternate energy source to the national economy before the end of the present century.

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GEOTHERMAL EFFLUENTS, THEIR TOXICITY AND PRIORITIZATION

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Exploitation of geothermal resources is hampered by a lack of understanding of the basic chemical interactions and toxicity hazards associated with the gaseous and aqueous effluents characteristic of various geothermal areas. The objective of this paper is the evaluation of the relative hazards of the various effluents in both liquid- and vapor-dominated fields in terms of concentration and chemical toxicity effects. Many chemical species must be considered in evaluating liquid-dominated systems, but only a few volatile species are significant in vapor-dominated systems. This is a direct consequence of the thermodynamic equilibria established among the chemical elements over the wide range of temperatures encountered in various geothermal areas. Vapor-dominated systems are lacking the aqueous phase required for dissolving water soluble salts. Since water is present as steam rather than as liquid, vapor-dominated systems tend to be lower in total dissolved solids than liquid-dominated systems. Volatility is the primary transport mechanism in vapor-dominated systems.

As might be anticipated from the preceding discussion, gas phase effluents are present in higher concentrations in vapor-dominated systems than in liquid-dominated systems. In the predominately vapor-dominated systems, such as The Geysers and Lardello, over 98 percent of the gas is steam. The remaining 2 percent is composed of gases including primarily hydrogen sulfide, carbon dioxide, methane, ethane, nitrogen, and hydrogen. Since water is a condensible gas at ambient temperatures, it is not normally listed although it is initially present in the gas phase. Typically only the noncondensible gases are listed as in Table 1.

Data for The Geysers are typical of the vapor-dominated systems which account for approximately 5 percent of the known geothermal resources. Wairakei is typical of the majority of the remaining 95 percent of the geothermal areas. Although the absolute concentrations of the noncondensible gases are quite different for the vapor- and liquid-dominated systems, the ratios are generally similar for those major species which are involved in the same chemical equilibrium systems. Carbon dioxide and water react to form carbonic acid which, in turn, can liberate hydrogen sulfide from metal sulfides. The complex chemical equilibria involving these and other species are temperature dependent and can be expected to be linear only over a narrow temperature range.

Ammonia, nitrogen, and hydrogen are involved in another chemical equilibrium reaction system by virtue of the following thermal dissociation:

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

Hydrogen is also contributed by the dissociation of water.

$$2H_2O \rightleftharpoons 2H_2 + O_2$$

Table 1. NONCONDENSIBLE GASES FROM GEOTHERMAL POWER PLANTS

	Concentration, (ppm)				
	Geyers[1]				Wairakei[2]
Gas	Mac	Min.	Max.	Ave.	Ave.
H_2S	10	5	1,600	222	40
	(0.03 Ca.) (0.01 Ill.)				
CO_2	-	290	30,600	3,260	600
CH_4	-	13	1,447	194	5
C_2H_6	-	3	19	-	1
NH_3	25	9.4	1,060	104	8
N_2	-	6	638	52	3
H_2	-	11	213	56	10

[1] Altshuler, 68th Annual Meeting of APCA, Boston, June 15-20, 1975.

[2] Axtmann, Science 187:795 (1975).

Thus, ammonia and nitrogen tend to occur at a ratio of about 10 to 1. Hydrogen ratios appear to be variable since hydrogen is contributed by two major sources, water and ammonia.

These constant ratio characteristics provide a valuable generalization for estimating the relative toxicity hazards of specific geothermal projects or areas on the basis of limited data.

The two noncondensible gases listed in Table 1 which present the greatest potential hazard are hydrogen sulfide and ammonia. Both exceed the maximum allowable concentrations by factors which cannot be ignored. The relative hazard of radon 222 and associated daughter products will be considered later. The global greenhouse effect associated with the evolution of carbon dioxide will not be considered because the magnitude is small compared with combustion sources.

Ammonia is primarily an upper respiratory poison. Inhalation of 1000 ppm causes irritation of the eyes and upper respiratory tract with coughing, vomiting, and redness of the mucous membranes of the mouth, nose, lips, and pharynx. Higher concentrations cause swelling of the lips and eyes, temporary blindness, restlessness, tightness in the chest, frothy sputum indicating pulmonary edema, and weak, rapid pulse. In geothermal operations ammonia is not likely to present a direct toxicity hazard except possibly in the immediate vicinity of the power plant. Ammonia toxicity risk is always small compared to that of hydrogen sulfide since it occurs at a much lower concentration. Atmospheric dilution would reduce the ammonia effluent levels to acceptable values very rapidly.

On the other hand, ammonia does present indirect hazards which have not received much attention to date in the evaluation of geothermal hazards. Ammonia is a base which reacts with acids such as hydrogen fluoride, sulfur dioxide, and hydrogen sulfide to form the corresponding salt. The resultant particulates are lower respiratory poisons which are generally more toxic than the original reactants and which, in addition, may settle out in given geographical areas depending upon local meteorological conditions. For example, ammonium sulfate particulates are approximately 5 times as toxic as sulfur dioxide. This is the basis for current concern and the basis for consideration of possible standards for sulfates. As is the case with many air pollutants, there is insufficient available evidence to prove that air pollution per se produces disease, but there are many indications that air pollution can aggrevate symptoms of pre-existing disease which may then prove fatal. Human beings with cardiovascular or respiratory disease appear to be particularly vulnerable. It is believed, however, that a particulate such as ammonium sulfate, not only has an adverse effect by itself, but is even more toxic when inhaled along with other common air pollutants. This synergistic effect of particulates formed from ammonia effluents may be a valid factor to consider in complying with requirements of the Significant Deterioration Act.

In addition to the human health hazards, the environmental impact on plant and animal species sensitive to changes in ammonium ion concentration and pH are likely to be significant. It has been postulated, for example, that the surface waters in some geothermal areas are neutral whereas equivalent waters in adjacent areas are slightly acid because of ammonia liberated from geothermal operations. Continuous operation could result in a shift in species distribution. Intermittent operation could result in a periodic change in pH which might have more significant environmental impacts.

The most noticeable geothermal effluent is hydrogen sulfide. The gas, which has a characteristic rotten egg odor even at very low concentrations, is known to cause irritation to the eyes and respiratory tract as well as deleterious effects to the nervous system of humans exposed to it (Ref. 1,2). In the immediate vicinity of the geothermal area, the hydrogen sulfide concentration far exceeds the maximum allowable concentration levels set by OSHA, federal, and state standards. The ambient air levels are high enough to fall within the concentration range where serious health effects and death have been well documented. Atmospheric dilution and possibly efficient scrubbing systems must be depended upon to reduce the ambient air levels to acceptable levels. Since geothermal operations are conducted in remote areas, adequate atmospheric dilution is easily achieved. On the other hand, atmospheric hydrogen sulfide emissions do pose a significant industrial hygiene hazard to workers in the immediate area. The fact that the OSHA limit of 20 ppm is exceeded by orders of magnitude cannot realistically be ignored. Hydrogen sulfide also has a major environmental impact on water quality as will be discussed later.

Hydrogen sulfide is much more toxic than is commonly realized. More concern is directed toward the odor nuisance than the health hazard. The human health and physiological effects of exposure to varying concentrations of hydrogen sulfide are presented in Table 2. As can be seen, the maximum concentration of 1600 ppm reported for The Geysers could result in death after only a brief exposure. The average value of 222 ppm reported for The Geysers is clearly within the range of serious health effects. Even the relatively lower hydrogen sulfide levels characteristic of liquid-dominated geothermal areas are well within the range of potential health hazard effects. Compliance with the 0.03 ppm limit set by California and other states will be difficult except at large distances from the geothermal site (Table 2).

As with most toxic chemicals, there is a wide variation in the individual response to hydrogen sulfide. It is well documented that persons who have consumed alcohol within the past 24 hours as well as psychotic or neurotic personalities are at high risk with respect to hydrogen sulfide. This is a majority rather than a minority of the American population (Table 3).

Alcoholics or individuals who have consumed alcohol within 24 hours of exposure have been overcome by unusually small concentrations of hydrogen sulfide (Ref. 3). Alcoholics may constitute a hypersusceptible population. Persons having psychiatric problems are a poor risk at any hydrogen sulfide level. Individuals with schizoid or paranoid tendencies

Table 2. HOW TOXIC IS HYDROGEN SULFIDE?

CONCENTRATION		EFFECTS
ppm	mg/m^3	
<0.067	<0.1	Odor nuisance
0.067-0.67	0.1-1	Loss of sense of smell
0.67-6.7	1-10	Eye irritation, fatigue
6.7-100	10-150	Eye irritation, photophobia after several hours
100-200	150-300	Eye and respiratory irritation within 1 hour, possible death within 48 hours
200-334	300-500	Eye and respiratory irritation within 30 min.; dyspnea, hemorrhage, and death with 48 hours; slight systemic effects within 4-8 hours
334-467	500-700	Slight systemic effects within 4 hours, hemmorrhage and death within 8 hours
467-600	700-900	Slight systemic symptoms within 1 hour, death within 4-8 hours
600-934	900-1400	Death within 1 hour

Table 3. HYDROGEN SULFIDE HIGH RISK POPULATIONS

HEALTH STATUS	SUPPORTING DATA
● Respiratory Illness	Poorly documented but probable
● Eye Infections	Poorly documented but probable
● Anemia	Not documented but possible
● Alcohol, past 24 hours	Well documented
● Psychotics, Neurotics	Well documented
● Repeated exposure	Controversial

become markedly worse following exposure. Neurotic individuals have developed innumerable bizarre symptoms, many of which remain for a long time as after-effects of the exposure (Ref. 3).

Other persons at high risk are those with respiratory illness, eye infections, and anemia. Although it is not well documented, the magnitude of additional risk could relate directly to the exposure of persons with respiratory illness to sulfur dioxide. Persons with anemia are presumed to be at high risk because hydrogen sulfide is known to react rapidly with oxyhemoglobin of the blood and thereby interfere with the body oxygen transport system.

Hydrogen sulfide is extremely toxic and is as rapidly fatal as hydrogen cyanide. Although it is a caustic irritant which reacts with the mucous membranes of the respiratory tract, the major and more serious toxic effect is paralysis of the respiratory center. The potential victim is deprived of a warning since even low concentrations paralyze the olfactory nerve. The principle route of absorption of hydrogen sulfide into the blood stream is through the lungs. High hydrogen sulfide concentrations cause almost instant paralysis of the entire central nervous system. Dissolved hydrogen sulfide exists only momentarily in the blood stream. It reacts with the oxygen of oxyhemoglobin to form thiosulfate and sulfate almost instantaneously. Hydrogen sulfide is prevented from accumulating in the body or acting as a cumulative poison by the very rapid detoxification process. Slow intravenous injection of several times the lethal dose of sodium sulfide has no apparent effect whereas a rapid injection of a much lower dose is fatal. (Ref. 4,5).

Systemic toxic effects result from absorption into the blood stream at a rate faster than it can be detoxified. This results in exposure of the central nervous system to the toxic effects of unoxidized hydrogen sulfide. The precise mechanism by which hydrogen sulfide exerts its toxic effects has not been firmly established, but it is generally agreed that enzyme inhibition results from the formation of sulfides of numerous cations. This reactivity removes enzyme metal cofactors required for optimal activity. This effect has been well established in laboratory investigations on numerous respiratory enzymes (Ref. 6,7,8) but has not been conclusively demonstrated in the body (Table 4).

Radon 222 is a radioactive gas which occurs in trace amounts in the noncondensible gases of geothermal effluents. The question of the relative radioactivity hazards associated with geothermal power plants is currently a topic of lively discussion. The discussions center around three major points:

- What is the concentration of radon 222 in the geothermal gas phase effluents?
- What are the concentrations of the radon 222 daughter products in the groundwaters?
- What is the radioactivity hazard of radon 222 and its daughter products relative to those of uranium 238 from nuclear power plants?

Table 4. TOXICOLOGY OF HYDROGEN SULFIDE

- Reacts with oxyhemoglobin to form thiosulfate or sulfate
- Tolerance depends on oxygen content of blood
  - Physical condition, hyperventilation, alcohol, asthma
- Detoxification is rapid
  - Dose vs. rate
  - Permanent vs. temporary effects
  - Subjective symptoms
- Lower respiratory poison
  - Humidity
- Not a cumulative poison

The reasons for the uncertainty regarding the adequacy of the geothermal experimental data and the subsequent interpretation of the significance of the data are illustrated in Table 5.

The emissions that accompany the disintegration of a radioactive element depend upon the rate at which the disintegration proceeds. This is commonly expressed in terms of the half-life of the radioactive element. For example, radium atoms show some 3 million times the activity of uranium atoms. This factor will have a different value for each radioactive element and will be large for those elements whose radioactivity is slight. A given amount of radium 226 will disintegrate into radon 222 at a rate that will remain practically constant over a period of several months because of the comparatively long half-life of radium 226. When formed, the radon 222 atoms will start to disintegrate into polonium 218 at a rate that is proportional to the number of radon atoms present and their tendency to disintegrate. At first this rate is slow since only a few radon 222 atoms have been formed. As radium 226 atoms continue to decompose, the number of radon 222 atoms disintegrating per unit time increases. Eventually, the rate at which radon 222 atoms are disintegrating will become equal to the rate at which they are being formed from radium 226. Then the amount of radon 222 will remain constant.

In such a series of radioactive elements in equilibrium, the amounts of each will remain constant.

Table 5. PRINCIPAL DECAY SCHEME OF THE URANIUM ELEMENTS

ELEMENT	MASS NUMBER	HALF-LIFE		ENERGY (MEV)	RELATIVE HAZARD* (α)	(β)
Uranium	238	$4.5x10^{9}$	years	4.2	1	
Thorium	234	24.1	days	0.19,0.10		(380)
Protactinium	234	69	sec.	1.18,2.31		($1.1x10^{7}$)
Uranium	234	$2.5x10^{5}$	years	4.76,4.71	$1.8x10^{4}$	
Thorium	230	$8.3x10^{4}$	years	4.68,4.62	$5.4x10^{4}$	
Radium	226	$1.62x10^{3}$	years	4.78	$2.7x10^{6}$	
Radon	222	3.82	days	5.49	$4.3x10^{11}$	
Polonium	218	3.05	min.	6.00	$7.7x10^{14}$	
Lead	214	26.8	min.	0.65		($4.9x10^{5}$)
Bismuth	214	19.7	min.	1.65,3.17		($6.6x10^{5}$)
Polonium	214	$1.64x10^{-4}$	sec.	7.68	$9x10^{20}$	
Lead	210	25	years	0.017		(1)
Bismuth	210	4.85	days	1.16		(1880)
Polonium	210	138	days	5.30	$1.2x10^{10}$	
Lead	206	Stable		-	-	-

*assuming equal radiation energy levels

Human illness due to industrial exposure to radon 222 and its daughter products is well documented. Radiation from radon 222 and its daughter products in metal mines in Joachimsthal, Czechoslovakia was found to be the cause of a sharp rise in lung cancer in 1949. Similar increases in the incidence of lung cancer have been reported in the United States uranium mining and milling industry (Ref. 9) and in fluorospar mining (Ref. 10).

Both concentration and half-life must be considered in assessing the relative radiation hazard of radon 222 and its daughter products in geothermal operations. This is always true; it is not unique to the geothermal situation.

For example, radon 222 is 4.3×10^{11} times as hazardous as uranium 238. Similarly, polonium 214 is 9×10^{20} times as hazardous as uranium 238. The following type of example illustrates the basis for current concern and uncertainty regarding the potential hazards associated with radioactive emissions from geothermal operations. Assume that equivalent radioactivity hazard criteria are applicable to both nuclear power plants and geothermal power plants. The limit for uranium concentration at the site boundary is usually taken to be 0.05 mg./meter^3. If radon 222 is 4.3×10^{11} times as hazardous as uranium 238, then the equivalent maximum allowable radon 222 concentration would be $0.05 / 4.3 \times 10^{11}$ or approximately 10^{-13} mg. Although the methodology in this example is correct, the conclusion is open to question because radon gas is not accumulated in the human body as is the case for uranium. However, if the same methodology is applied to polonium 218, a radioactive daughter product of radon 222, the logic is totally correct and the comparison of relative hazard is valid. In the case of polonium 214, the equivalent maximum allowable concentration would be $0.05 / 9 \times 10^{20}$ or 5×10^{-23} mg.

As can be seen from Table 5, the same situation is true in varying degrees for all of the other daughter products of radon 222. All are relatively more hazardous than uranium 238 in varying degrees.

In this radiochemical hazards analysis no distinction has been made between the relative hazards of alpha, beta, and gamma radiation or the energy levels of the specific radioisotopes. Relative hazard ratings have been subdivided and treated separately in Table 5 but cross-comparisons were not attempted.

Externally, alpha particles do not penetrate the skin. However, when given off internally after ingestion or inhalation, they produce serious damage because the energy content is completely absorbed.

High energy beta rays can penetrate the protective layers of the skin but usually do not reach deep-seated organs when delivered externally. When ingested or inhaled, they often produce more wide-spread damage than alpha emitters.

This type of analysis suggests that a thorough examination of the concentrations of radon 222 in the geothermal non-condensible gas phase as well as the concentrations of the other non-volatile daughter products in the aqueous phase may be warranted. This is not a simple problem. Many of the daughter products of radon 222 are present at concentration levels far below the levels detectable by conventional analytical methods. Only the most highly sophisticated chemical and radiochemical trace metal methods are capable of yielding significant results.

In all geothermal operations, but particularly in those involving liquid-dominated fields where the volume and concentration of the geothermal fluids is high, water quality problems related to total dissolved solids and dissolved heavy metals is a major problem. Although the absolute concentrations of the individual trace elements may vary within a given area, the ratios of the constituents are generally similar. The concentration of the solution is the primary variable. The composition of the solution is relatively constant (Table 6).

These are valuable generalizations to keep in mind during the sampling and analysis of geothermal waters and associated trace metals. For example, assume an initial sample of the initial composition and dilution as given in Table 7.

The extent of dilution determines the sample size and analytical method required to determine the chemical composition. In the case of very diluted geothermal fluids, valid chemical analysis of the trace metal content can be achieved only by use of the most sensitive analytical methods or by sufficient sample concentration prior to analysis. Much of the uncertainty related to assessing the toxicity hazard of geothermal

Table 6. GEOTHERMAL FLUIDS

- Chemical Composition Varies With
  - Temperature, pressure
  - Geology
  - Vapor- vs. liquid-dominated

o Within a Given Area
  - Absolute concentrations vary
  - Ratios of constituents are similar

Table 7. HYPOTHETICAL EXAMPLE OF DILUTION EFFECT

COMPONENT	CONCENTRATION, PPM Initial	Dilute 1/1k	Diluted 1/1M
Na	300,000	300	0.3
Cl	300,000	300	0.3
Mn	2,000	2	-
B	800	0.8	-
Pb	400	0.4	-
F	20	0.02	-
Hg	0.01	-	-

fluids stems from the practice of reporting "nil" as the concentration of a trace metal without specifying the lower limit or accuracy of the analytical method. As can be seen from Table 7, the conclusions regarding toxicity are quite different depending on the particular set of data used. These data may be adequate for preliminary engineering design but are inadequate for toxicity evaluation.

Engineering data of this type are given in Table 8. As can be seen, it is difficult to evaluate the potential hazard for most of the heavy metals. Taking lead as an example, numerical data are reported only for the most concentrated brine from the Niland area. This presentation of data leads to the conclusion that lead may be a toxic hazard at Niland but not at The Geysers or Cerro Prieto. As will be shown later, this is not necessarily a valid conclusion.

In most cases, evaluation of relative toxicity hazards requires consideration of worst case conditions and an assessment of average operating conditions and the probability of occurrence. A worst case example for the Imperial Valley area is presented in Table 9. This Table lists the maximum value reported for each chemical species in any geothermal well in the area. This is an unrealistically severe worst case example from the point of view of environmental assessment of the Imperial Valley area. The probability of any one geothermal well having all of the listed high concentrations is very low. This type of presentation was chosen because it permits presentation of all of the potentially toxic chemical species in a single table.

Table 8. COMPOSITION OF GEOTHERMAL FLUIDS (Ref. 11)

Component	Parts per million by weight		
	The Geysers, California	Cerro Prieto, Mexico	Niland, California
Sodium	.12	5,610	53,000
Potassium	.10	1,040	16,500
Calcium	.20	321	27,800
Lithium	.002	14	210
Magnesium	.06	Negative	10
Strontium	.10	28	440
Barium	--	57	250
Rubidium	--	--	70
Cesium	--	--	20
Iron	--	--	2,000
Manganese	--	--	1,370
Lead	--	--	80
Zinc	--	--	500
Silver	--	Trace	--
Copper	--	Trace	--
Silicon dioxide	.50	--	400
Chlorine	20.00	9,694	155,000
Boron	.10	12	390
Fluorine	.10	Trace	--
Sulfur	7.10 (sulfate)		
Total dissolved solids	28.38	17,000	259,000
Ammonium	236.0		
Bicarbonate	775.0		

Table 9. TRACE METALS IN GEOTHERMAL FLUIDS - A WORST CASE EXAMPLE*

		Water		Air	
Component	Max.Conc (ppm)	Public Supply (mgm/1)	Rel.Haz.	TLV mgm/m^3	Rel.Haz.
Silver	3	0.001	3,000 X	-	-
Arsenic	15	0.05	150 X	0.25	300 X
Barium	570	1.0	570 X	0.5	5,700 X
Cobalt	0.4	-	-	0.5	4 X
Chromium	1.8	0.05	36 X	0.1	90 X
Cesium	22	-	-	-	-
Copper	10	1.0(taste)	10 X	-	-
Iron	4200	0.3(taste)	14,000 X	-	-
Mercury	0.008	0.002	4 X	0.1	0.4 X
Manganese	2000	0.05	40,000 X	5.0	2,000 X
Lead	400	0.05	8,000 X	0.2	10,000 X
Rubidium	168	-	-	-	-
Antimony	0.5	-	-	0.5	5 X
Tin	0.65	-	-	-	-
Strontium	740	-	-	-	-
Thallium	1.5	-	-	0.1	75 X
Vanadium	6	-	-	0.1	300 X
Zinc	970	5.0(taste)	194 X	-	-
Bromide	146	-	-	-	-
Iodide	22	-	-	-	-
Ammonium	570	0.5	1,140 X	-	-
Nitrate	35	10.0	3.5 X	-	-
Fluoride	18	1.4-2.4	8-13 X	2.5	36 X
Boron	745	-	-	-	-
		(Irr.0.75-2.0)	(373-1000X)		

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*Geothermal Wastes and the Water Resources of The Salton Sea Area, Dept. of Water Resources Bulletin No. 143-7 (February 1970).

Maximum concentrations of each species are evaluated in terms of relative hazard with respect to public water supply and air quality criteria. In a complete study, all applicable criteria would be evaluated in a similar manner. The relative hazard was calculated by dividing the maximum concentration observed by the appropriate limit. This gives a number which indicates how much any given value exceeds the maximum allowable concentration.

Manganese, lead, and silver appear to be potentially the most serious water toxicity hazards on the basis of this set of data. The other components such as arsenic, barium, chromium, ammonium ion, nitrate, and fluoride cannot be ignored but relatively speaking are a lesser hazard than manganese, lead, and silver which occur at much higher concentrations. Boron is essentially nontoxic to humans but is toxic to plants. Although any mercury is bad, the relatively small concentrations indicated by these data indicate that it may be a lesser problem relative to some of the others. The question of mercury toxicity limits is currently a subject of active concern; the ultimate assessment in geothermal operations will be determined by the established regulatory limits as well as by more accurate analysis of geothermal fluids and gases.

Chronic manganese poisoning has not been as extensively investigated as lead and mercury, but the physiological effects are similar to those of the other heavy metals. Manganese is primarily a central nervous system poison. It affects the large ganglion cells of the cortex and the mid-brain. The symptoms are acute anxiety, compulsive behavior, hallucinations, and physical disorientation.

Silver poisoning was common at the beginning of the century from the inclusion of silver compounds in cosmetics. Although fatal poisoning is not a likely possiblility, continued exposure to soluble silver salts leads to a permanent blue-black discoloration of the skin and eyes. Although soluble silver salts may cause local corrosive effects, they are not likely to produce systemic effects because silver ion is precipitated by protein and chloride.

The physiological effects of other potentially toxic water pollutants will not be discussed in this paper. The reader is referred to "Handbook of Poisoning" by Robert H. Driesbach, Lange Medical Publications, Los Altos, Calif. for an excellent source of toxicological and physiological information in summary form.

When evaporated to dryness as in waste disposal areas or from spillage in work areas, the dust and particulate matter may produce an air quality problem. Generally, the inhalation of dust and particulates is a more serious human health hazard than direct ingestion. For this reason, maximum allowable concentrations in air as well as in water should be considered.

It is significant to note that the relative hazards in air are not the same as in water. The particulate components most hazardous with respect to inhalation are lead, manganese, and barium. Several others, including fluoride, vanadium, thallium, chromium, and arsenic, would be considered to be at dangerous levels if they were encountered in urban air samples. As was the case for noncondensible gases and radon radioactive decay products, it is important to consider the relative toxicity hazard both in terms of industrial hygiene where the primary consideration is safety of workers and in terms of the safety of surrounding communities after dilution or scavenging.

The sulfur cycle presented in Table 10 summarized the chemical fate of hydrogen sulfide in the environment. It is converted to sulfur dioxide, sulfur trioxide, sulfuric acid, or particulates within a matter of hours or, at most, a few days. The particulates are metal sulfides or metal sulfates. The mere fact that hydrogen sulfide values drop to low levels within a short time and distance from the geothermal site does not necessarily mean that the hazard is less. The nature of the hazard has been transformed to that of the new chemical species.

In summary, it is appropriate to discuss the potential health hazards associated with geothermal power plants in a broader perspective. Hydrogen sulfide is a chemically reactive gas. It will not remain in the form of hydrogen sulfide for long time periods as shown in Tables 11 and 12.

Table 10. SULFUR CYCLE

AIR POLLUTION

$$H_2S \xrightarrow{O_2} SO_2 \xrightarrow{\text{Sun}} SO_3 \xrightarrow{H_2O} H_2SO_4$$

CONCENTRATION MECHANISM

$$H_2S + \text{Metals} \longrightarrow \text{Metal Sulfides} \downarrow$$

$$(NH_4)_2S, PbS, Fe_2S_3, HgS \text{ etc.}$$

WATER POLLUTION

$$\text{Metal sulfide} \downarrow \xrightarrow{OH^-} \text{no reaction}$$

$$\text{Metal sulfide} \downarrow \xrightarrow{H^+} \text{metal ion} \uparrow + H_2S \uparrow$$

Table 11. ULTIMATE FATE OF GEOTHERMAL EFFLUENTS*

ELEMENTAL COMPOSITION	CONTRIBUTED BY	CONCENTRATION (ppm)	
		INITIAL	EQUILIBRIUM
H_2	H_2,NH_3	87	-
S	H_2S	209	-
N_2	N_2,NH_3	142	233
O_2	CO_2	436	150
SO_3		-	238
$H_2SO_4(1)$		-	253

*Equilibrium thermodynamic gas composition calculated for an average Geysers noncondensible gas composition (222 ppm H_2S, 3260 ppm CO_2, 104 ppm NH_3, 52 ppm N_2, and 56 ppm N_2) with Woodward-Clyde Consultants Air Chemistry Computer Program.

Table 12. ULTIMATE FATE OF GEOTHERMAL EFFLUENTS IN HUMID ATMOSPHERE

ELEMENTAL COMPOSITION	CONTRIBUTED BY	COMPOSITION (ppm)	
		INITIAL	EQUILIBRIUM
H_2	H_2,NH_3,H_2O	300	-
S	H_2S	209	-
N_2	N_2,NH_3	142	233
O_2	CO_2,H_2O	436	350
$H_2SO_4(1)$		-	504

*Equilibrium thermodynamic gas composition calculated for the average Geysers noncondensible gas composition (Table 11) plus 213 ppm H_2O with Woodward-Clyde Consultants Air Chemistry Computer program.

Even more important, a mechanism exists for the chemical concentration of toxic heavy metals as their water insoluble sulfides or sulfates. The particular geographical sites of concentration depend on the meteorology and hydrology of the region. In general, both the heavy metal sulfides and sulfates will remain insoluble and consequently immobilized as long as they are in alkaline soils or water. Thus, although hydrogen sulfide is not a cumulative poison and is not concentrated significantly in the biosphere, it indirectly functions as a concentration mechanism. However, if the region in which they are accumulated becomes acidic, high concentrations of toxic heavy metals and hydrogen sulfide will be released at some later date. Geothermal accumulation areas can become acidic in a number of ways including, for example, diversion of water courses, inadvertent industrial waste disposal, or intentional addition of chemical soil additives, such as calcium sulfate. A significant number of toxic episodes involving heavy metals and sulfides have occurred in this way.

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ADDITIONAL DISCUSSION OF THE NONEQUILIBRIUM REACTIONS OF H_2S PRESENTED AT THE LAKE COUNTY GEOTHERMAL SEMINAR

The rate of conversion of hydrogen sulfide to thermodynamically stable end products can be calculated by means of a nonequilibrium air chemistry computer program. This program is analogous to a photochemical smog model except that it was written to consider up to 36 elements . Thus, it has the capability of considering photochemical reactions of sulfur species as well as carbon, hydrogen and oxygen.

This program indicates that hydrogen sulfide is converted to sulfur dioxide, sulfur trioxide and sulfuric acid rapidly. The rate of conversion varies between 3 and approximately 24 hours depending on humidity, temperature and sunlight intensity. Within the context of geothermal emissions, this means that hydrogen sulfide with an air quality standard of 0.04 ppm in California is rapidly converted to sulfuric acid which does not have an established legal limit. It is highly probable that the rapid conversion of hydrogen sulfide to other products is part of the reason why field measurements do not detect significant quantities at distances remote from the site boundary.

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SOME PROBLEMS INVOLVED WITH SAMPLING GEOTHERMAL SOURCES

by

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ABSTRACT

Geothermal wells must be sampled for a variety of purposes including geologic and geochemical interpretation, engineering design of facilities, environmental release evaluation, and documentation of baseline conditions. Basic factors influencing the choice and application of sampling methods are reviewed including the type of the geothermal resource, the analyses of interest, well production parameters, utilization processes, and possible sample contamination or instability. Three basic methods of sampling are described including condensation, phase separation, and use of evacuated containers. Several practical problems experienced by various workers are discussed. These include the natural variability of fluid composition with time, effects of well-bore heat losses, effects of well flow rate and production time, sampling locations, laboratory simulation studies, contamination by corrosion reactions, and documentation of hydrologic systems possibly connected to the geothermal resource.

I INTRODUCTION

Discharges from geothermal sources must be sampled and analyzed for a variety of purposes. Knowledge of the physical and chemical nature of geothermal fluids is necessary for understanding the geologic and geochemical conditions of the natural resource, for designing equipment and processes to utilize the resource, for anticipating and evaluating potential environmental releases or required controls, and for documenting baseline conditions which may change during the period of resource extraction.

The unique aspects of geothermal sources, especially high temperatures and pressures, impose constraints on the methods of sampling. This presentation provides a review of some factors important in selecting and applying sampling methods to geothermal discharges. Some examples of practical problems are included to suggest sampling difficulties encountered in certain situations. The need to collect and use information about related hydrologic systems is discussed in the context of a case study.

II SAMPLING METHODS

A. General Considerations

A variety of sampling techniques have been applied to discharges from thermal sources. Finlayson[1] reviewed literature on methods for collecting and analyzing volcanic and hydrothermal discharges. The basic methods included air displacement, liquid displacement, vacuum tubes or flasks, condensation, and adsorption. Most of the methods were applicable to sampling vents, fumaroles, bubbling hot springs, or other natural openings. The methods preferred for collecting steam condensate from geothermal boreholes involved condensation and the use of evacuated flasks. Another technique is the separation of liquid and vapor.

The choice of a sampling technique requires consideration of the type of fluid to be collected and the analyses which will be performed. The fluid may be liquid or gas or a two-phase mixture depending on the type of geothermal resource and pressure-temperature conditions. A vapor reservoir will yield either saturated or slightly superheated steam containing some fraction of non-condensable gases. A hot liquid reservoir could produce either a pressurized liquid with some dissolved gases, or a two-phase flow of steam and entrained water if pressure-temperature conditions permit flashing. No natural fluids will be present in a hot dry rock resource prior to injection of water, but it will probably contain pressurized liquid when operational.

The analytical methodology may impose constraints on sampling technique. Sample size may be important when analyzing for minor gaseous or dissolved constituents. Analysis for gases such as CO_2 and H_2S may require preconditioning in the sample container to control solubility.

Some solids such as silica may precipitate on cooling requiring predilution of the sample. Constituents with a propensity for adsorption such as mercury require careful consideration of materials used in sampling apparatus.

Effluent streams from a facility using geothermal fluids may or may not require sampling methods similar to those used for wells. For example, the steam-gas mixture from noncondensable gas ejectors could be sampled by techniques applicable to steam wells. However, the cooled condensate from a power plant could be sampled by more conventional water sampling techniques.

The possibility of samples becoming contaminated or otherwise changing after collection requires special precautions. Samples may be contaminated during the collection process by such things as inadequate flushing of connectors, lines, or containers. Corrosion reactions in the well casing can contribute gases or dissolved materials. Formation fluids may be contaminated for some time after completion by drilling fluids. Changes in sample composition can result from precipitation, adsorption, permeation of gases through containers, radioactive decay, or chemical reactions between constituents in the sample.

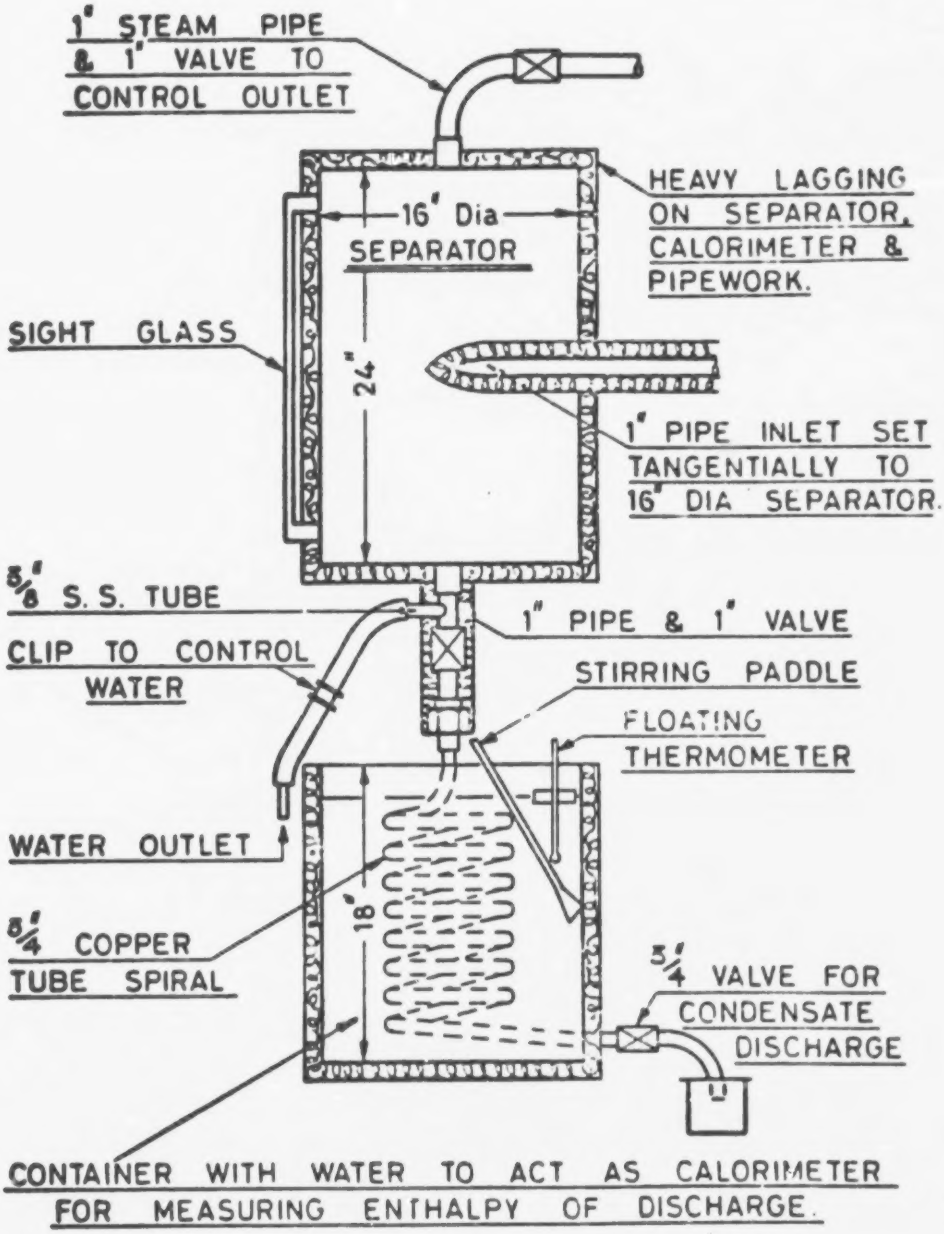
B. Examples of Sampling Methods

Three basic techniques depending on separation of phases, condensation, and the use of evacuated containers have been used to sample fluids from geothermal wells. An indirect laboratory simulation technique has been used to obtain predictive information for a hot dry rock geothermal resource.

1. Separation of Phases

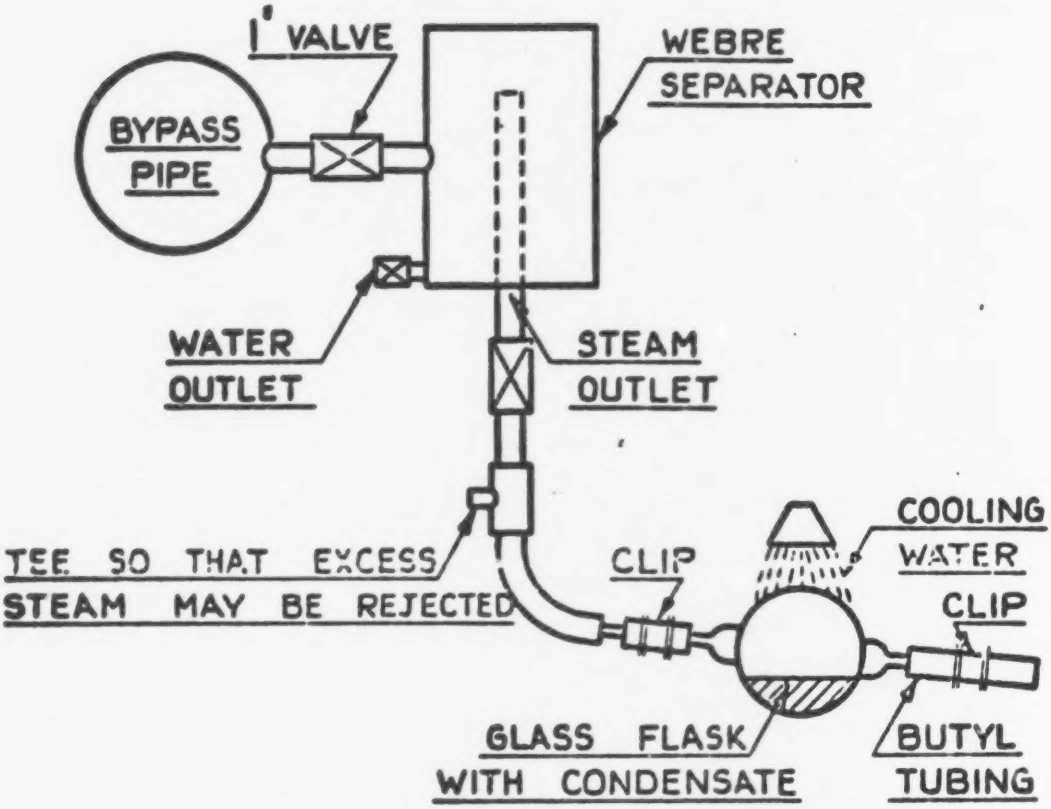
Liquid-vapor separation has been employed at the Wairakei geothermal field in New Zealand.[2,3] A simple separator (Figure 1) operating at atmospheric pressure is used for sampling low pressure (30-40 psig) two phase flow. A calorimeter is used to measure the enthalpy of the discharge so separate results from steam and water analyses can be related to concentrations in the total flow. High pressure (>100 psig) samples are taken using small Webre separators (Figure 2) which have very small pressure drops. Steam samples are condensed in evacuated glass flasks cooled by water. The flasks may be partly prefilled with alkaline solution to absorb CO_2 and H_2S for laboratory analysis by titrations. Water samples are collected after passing the hot pressurized water through a cold-water jacketed pipe.

A unique advantage of this method is the capability to obtain separate samples of the liquid and vapor phases. Disadvantages include the need for careful control of heat losses in the equipment so as not to alter the steam/water ratios.


1" STEAM PIPE
& 1" VALVE TO
CONTROL OUTLET
HEAVY LAGGING
ON SEPARATOR,
CALORIMETER &
PIPEWORK.
16" Dia
SEPARATOR
SIGHT GLASS
24"
1" PIPE INLET SET
TANGENTIALLY TO
16" DIA SEPARATOR.
5/8 S. S. TUBE
1" PIPE & 1" VALVE
CLIP TO CONTROL
WATER
STIRRING PADDLE
FLOATING
THERMOMETER
WATER OUTLET
18"
3/4 COPPER
TUBE SPIRAL
3/4 VALVE FOR
CONDENSATE
DISCHARGE
CONTAINER WITH WATER TO ACT AS CALORIMETER
FOR MEASURING ENTHALPY OF DISCHARGE.

LOW PRESSURE SEPARATOR SAMPLING APPARATUS

FIGURE 1


1" VALVE
WEBRE SEPARATOR
BYPASS PIPE
WATER OUTLET
STEAM OUTLET
COOLING WATER
TEE SO THAT EXCESS STEAM MAY BE REJECTED
CLIP
CLIP
GLASS FLASK WITH CONDENSATE
BUTYL TUBING

HIGH PRESSURE SEPARATOR SAMPLING APPARATUS

FIGURE 2

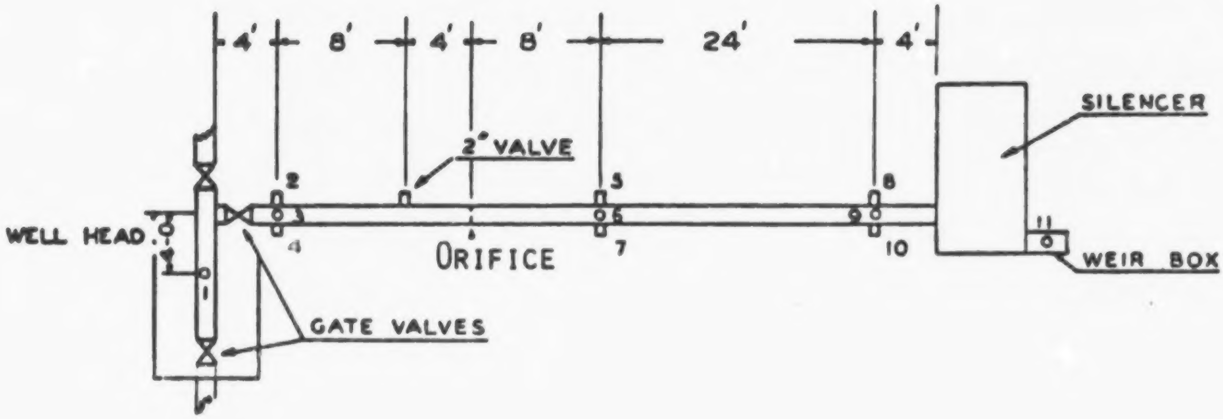
The location at which samples are taken from the wellhead and associated delivery system piping can influence sample composition. Differences in steam/water ratios, pressure, and velocity can all be particularly important when sampling two-phase flow. Mahon has discussed such problems encountered at Wairakei.[3] Table I (from Ref. 3) presents data from various sampling points on a wellhead and by-pass line incorporating an orifice constriction as illustrated in Figure 3. The numbered points identify the sampling locations. All sampling locations upstream of the constriction give consistent results. Downstream from the constriction, the pressure drops and some water flashes to steam resulting in reduced CO_2/steam ratios at points 6 through 10. It is possible to relate the CO_2 to total discharge in a consistent manner for all points except number 7 by knowledge of the enthalpy. Mahon suggests that after passing through the constriction a proportion of the water in the discharge is thrown to the top of the pipe resulting in poor sampling conditions for some distance downstream as indicated by the irregularities at points 5, 6, and 7. About 30 feet downstream, at points 8, 9, and 10, representative steam samples could be obtained but most of the water was evidently at the bottom of the pipe (Ref. 3).

Similar problems can occur in steam well and steam line sampling if there are points at which heat losses cause condensation. Each different configuration requires evaluation

TABLE I

SELECTION OF RESULTS OBTAINED FROM SAMPLING UNDER CONSTRICTED BY-PASS CONDITIONS

SAMPLING POINT	PRESSURE (PSIG)	CL IN WATER (PPM)	CO_2 IN STEAM (MILLIMOLES/ 100 MOLES H_2O)	CO_2 IN TOTAL DISCHARGE (MILLIMOLES/ 100 MOLES H_2O)
1	198	2 287	65.2	6.1
1	198	2 287	65.4	6.1
2	180	2 249	62.9	6.5
2	180	2 249	61.9	6.4
3	180	2 289	62.0	6.4
3	180	2 289	62.8	6.5
4	180	2 266	62.9	6.5
4	180	2 266	62.9	6.5
5	40	2 231	SEPARATOR FLOODED	
6	40	2 228	30.4	6.8
7	40	1 639	16.0	3.2
8	28	1 008	29.2	6.3
8	28	549	28.6	6.2
9	28	1 052	29.2	6.3
9	28	1 067	29.0	6.3
10	28	2 019	28.7	6.2
10	28	2 056	29.4	6.4
11	WEIR BOX	2 284	---	---


4'
8'
4'
8'
24'
4'
SILENCER
2" VALVE
2
5
8
WELL HEAD
3
6
9
1
4
ORIFICE
7
10
11
WEIR BOX
GATE VALVES

SAMPLING LOCATIONS

FIGURE 3

of factors that could degrade the representativeness of the sample.

2. Condensation

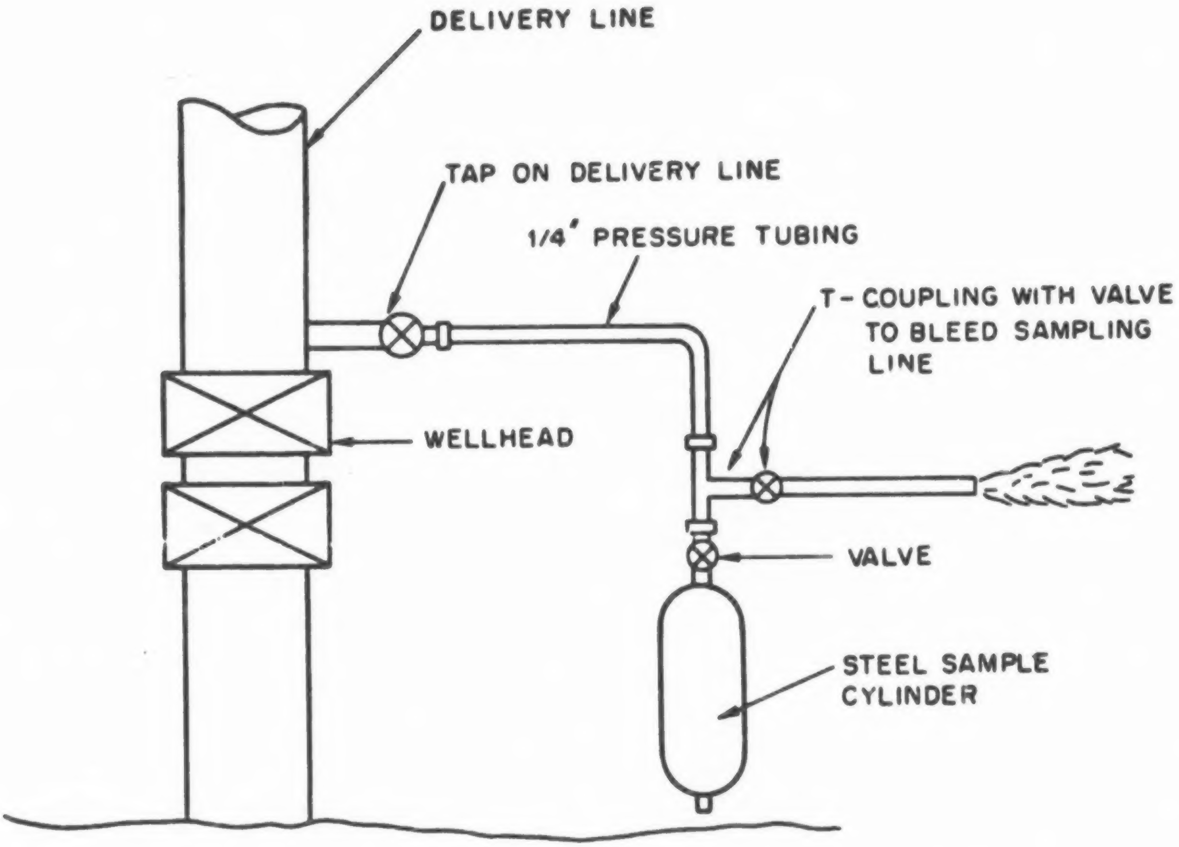
Sample condensation is accomplished by directing a portion of the discharge through a condenser to completely convert steam to liquid or reduce the temperature of water so no flashing will occur. The condenser may be a coil of metal tubing, such as aluminum or stainless steel, immersed in a container of water or ice or a finned air heat exchanger. At the outlet of the condenser the liquid and noncondensable gas portions can be collected and handled in different ways. Barnes, et al.,[4] collected the liquid in plastic bottles. Some portions were filtered and then acidified for analyses of cations or left untreated for analyses of other components. Noncondensable gases were collected by displacing condensed water from plastic syringes, and the sealed syringes were transported to the laboratory submersed in the condensate to avoid gas diffusion through the plastic. The gases were analyzed by gas chromatography.

Alternatively, the output of the condenser can be directed to an interconnected sampling train. The train could include containers for accumulating the condensate, others partly prefilled with alkaline solution for removing CO_2 and H_2S or lead acetate solution for reacting H_2S, and a flask for collecting remaining noncondensable gases.

The basic method is applicable to single-phase or two-phase flows where total discharge analysis is of interest. An advantage of the method is that almost any desired size of sample can be obtained. If gases are separated in the field the possibility of reactions prior to analysis is reduced. Cooled liquids are immediately available for field determinations of critical parameters such as pH. Disadvantages include the need for considerable equipment and availability of cooling water or ice in the field.

3. Evacuated Containers

Evacuated containers can be used for sampling total discharge. An evacuated pressure cylinder can be connected directly to a tap on the wellhead or delivery line (Figure 4). A "T" fitting with a valve and bleed line permits purging of air from the connecting line and fittings. The sample size can be controlled by the time allowed for flow into the container, or by inducing additional condensation in the container through cooling with water. Certain precautions are necessary. If pressure equilibrium is reached between the container and delivery line, continued condensation of steam can displace non-condensable gases out of the container. If the inlet to the container is at the bottom, liquid may be able to drain back into the connecting line. As the sample cools, the contents of the cylinder will be at less than atmospheric pressure requiring tightly sealed fittings to avoid atmospheric contamination.


DELIVERY LINE
TAP ON DELIVERY LINE
1/4" PRESSURE TUBING
T- COUPLING WITH VALVE TO BLEED SAMPLING LINE
WELLHEAD
VALVE
STEEL SAMPLE CYLINDER

EVACUATED CYLINDER SAMPLING APPARATUS

FIGURE 4

Non-condensable gases can be removed from the container for analysis by direct pumping or by introducing inert carrier gases to strip dissolved gases from the liquid. The liquid portion of the sample can be drained after pressure equilibration.

The technique has been applied to single-phase liquid or vapor flow with reproducible results.[5,6] For two-phase flow reproducibility was poor, possibly because of the constantly decreasing flow rate through the connecting line as pressure builds up in the container.[5]

The technique has the advantage of being simple to use in the field. Disadvantages include possible reactions before laboratory analysis. The use of metal cylinders may be problematic when corrosion reactions are possible or when minor elements are of interest. Without induced condensation, the sample size may be small, making some anslyses difficult.

4. Laboratory Simulation

The Hot Dry Rock Geothermal Source Demonstration experiment being conducted by the Los Alamos Scientific Laboratory presents a unique problem to source sampling. The geologic system from which energy is to be extracted contains no naturally present fluids. Two holes are to be completed at a depth of about 3000 m (10,000 feet) in granitic basement rock and connected by hydraulic fracturing. Then water will be circulated in a pressurized loop to extract heat from the 200°C. formation.

Thus it is necessary to resort to simulation studies in the laboratory to obtain an indication of dissolved materials that will be dissolved by the circulating fluid.

Cores from the zone to be fractured were taken during drilling. These rock samples have been used in both flowing and non-flowing laboratory experiments at the pressure and temperature conditions expected to occur during the in-situ circulation experiments. Preliminary results indicate that there will not be any evolution of gases. Dissolved constituents are apparently subject to change with time because of differential dissolution rates for various mineral types and because of reprecipitation of certain compounds controlled by complex geochemical equilibria.[7,8] The laboratory simulation results will provide an indication of what materials may be of importance in planning waste disposal operations and environmental monitoring.

III Factors Affecting Fluid Composition During Sampling

A. Natural Variability

An indication of the possible importance of natural variability in fluid composition is implicit in data for sequential samples taken from steam wells during different periods. Figure 5 shows the time dependence of three constituent ratios measured in five samples collected during a 24-hour period.[5] The flowrate of the well was

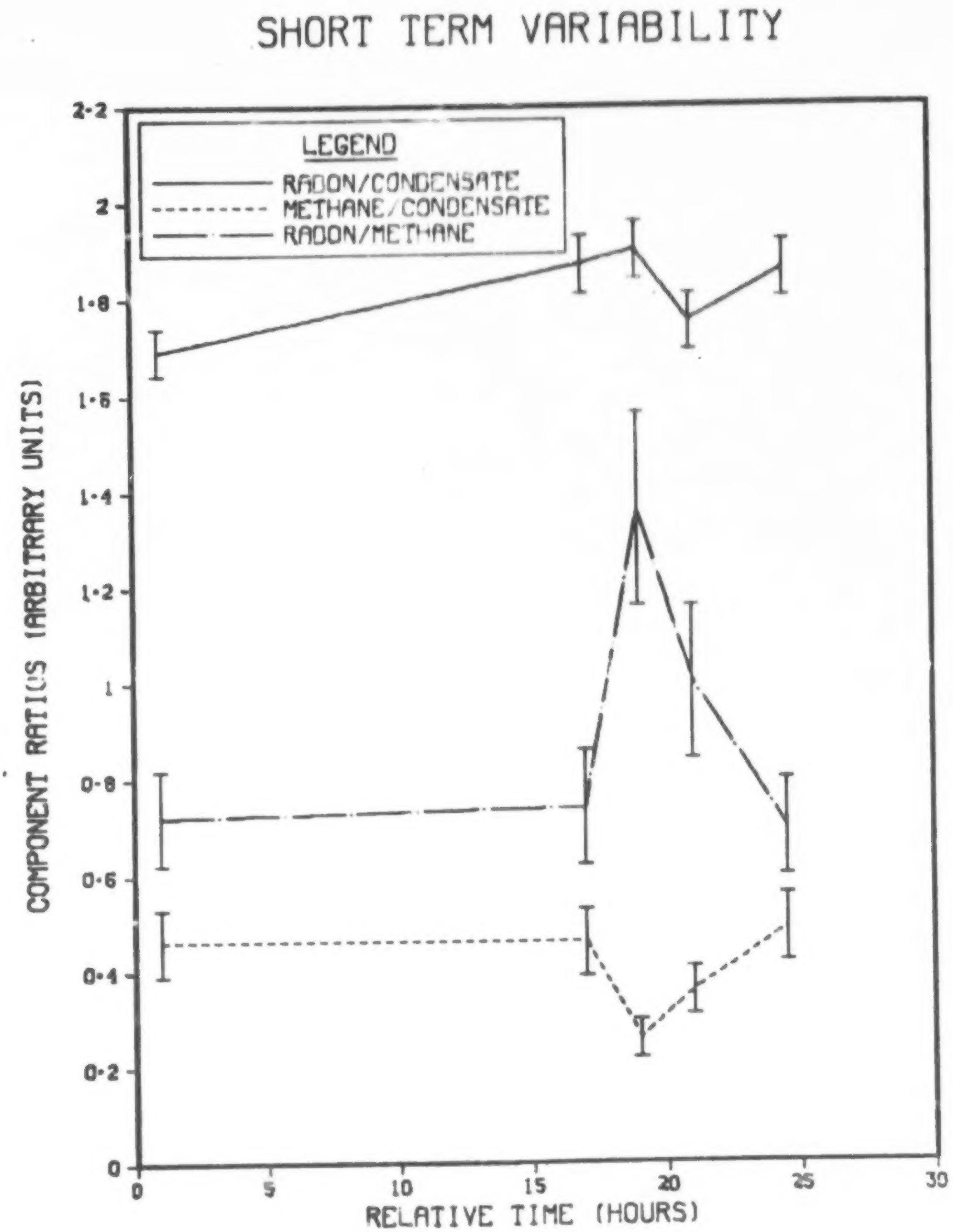

SHORT TERM VARIABILITY

FIGURE 5

constant within about 1.5% of the average during the period. The total variation of the Rn/Condensate ratio was about 10%, or roughly twice the standard deviation of about 4% expected for individual measurements. The ratios of CH_4/Condensate and Rn/CH_4 each cover a range with a factor of about 2 between the lowest and highest values. Individual measurements had standard deviations of about 15%.

Barnes, et al.,[4] reported a difference in CO_2 and CH_4 contents of samples from steam wells taken 7 days apart. The ratio of CO_2/CH_4 varied by a factor of almost 5 for one of the wells.

A longer test reported by Kruger and Umana[6] showed variation in the Rn/condensate ratio measured in 18 samples collected during a 20-day period. The left-hand portion of Figure 6 shows the dependence of the ratio with time while the steam well was flowing at a constant rate of about 100,000 kg/hr (∿200,000 lb/hr). The extreme values are about 28% lower and 32% higher than the average.

These few examples are sufficient to indicate that variability of fluid composition may be a significant consideration when establishing a sampling program for many constituents in geothermal fluids. Variability may be due to inhomogeneities in the reservoirs, geochemical changes, or geologic and hydrologic changes.

B. Well Production Conditions

1. Well Flowrate

The radon content of geothermal steam discharges can change significantly at different flowrates. Referring again to Figure 6, it can be seen that the Rn/Condensate ratio was higher during the 20-day period when the flowrate was about 100,000 kg/hr ($\sim$200,000 lb/hr) than during the 28-day period after the flowrate of the well was dropped to about 50,000 kg/hr ($\sim$100,000 lb/hr). Following a transient, the average Rn/condensate ratio measured in the last 5 samples was about 50% of the average measured in samples collected at the higher flowrate. Kruger and Umana[6] suggest that this flowrate dependence of the Rn/Condensate ratio may be explained by different flowtimes which permit different decay periods for the radon, or by different emanating power in the different flow volumes swept out around the well bore at the two rates.

It is possible that similar effects may occur for other non-condensable gases or for dissolved constituents. One of the authors has observed an increase in the concentration of some trace elements in water wells when they are pumped at lower rates. A possible but as yet unverified explanation is that certain zones in the aquifer with different chemical and hydrologic characteristics contribute varying proportions of the total flow at different drawdown conditions. Similar variations may be important for geothermal wells.

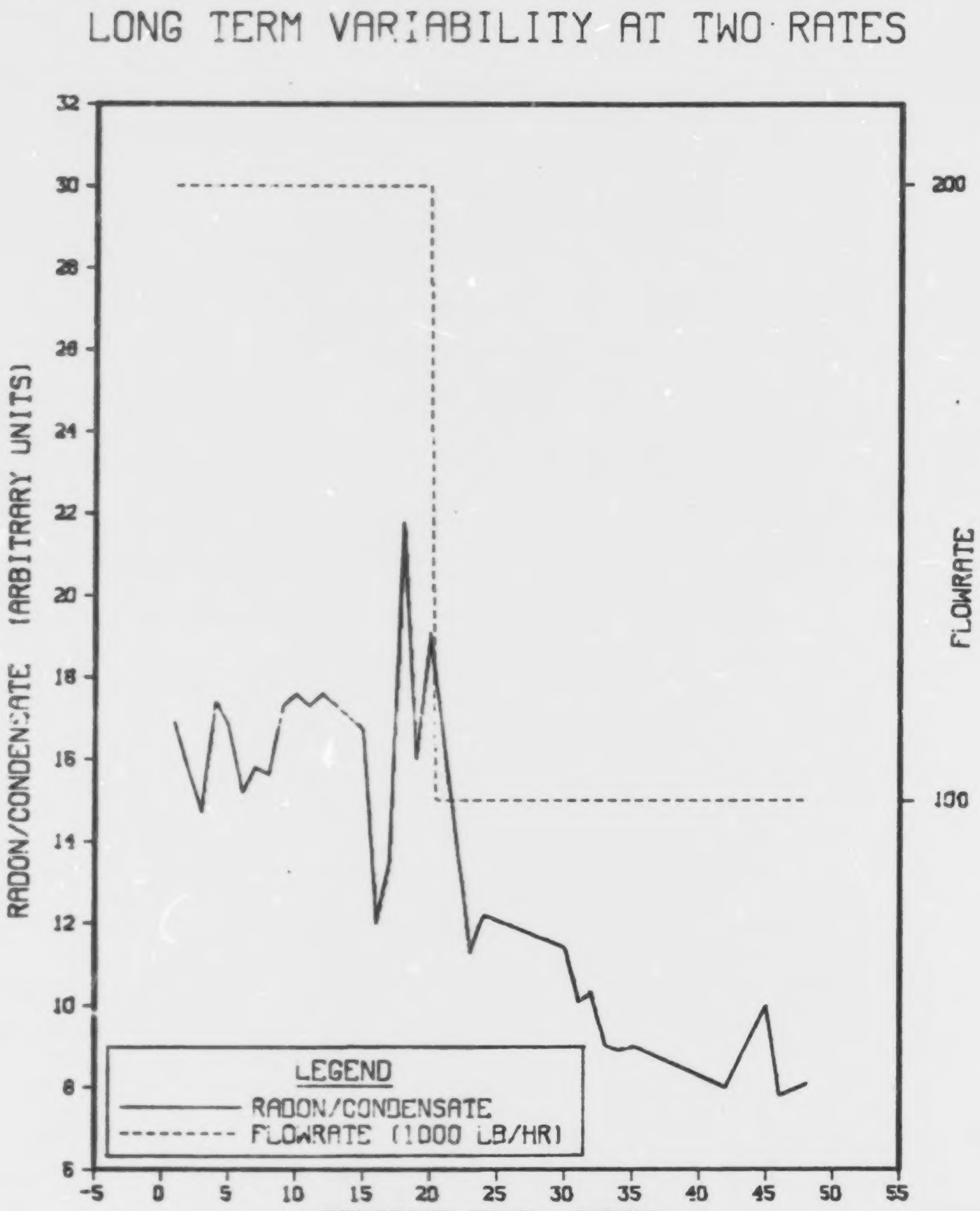

LONG TERM VARIABILITY AT TWO RATES
RADON/CONDENSATE (ARBITRARY UNITS)
32
30
28
26
24
22
20
18
16
14
12
10
8
6
FLOWRATE
200
100
-5
0
5
10
15
20
25
30
35
40
45
50
55
RELATIVE TIME (DAYS)
LEGEND
RADON/CONDENSATE
FLOWRATE (1000 LB/HR)

FIGURE 6

2. Wellbore Heat Losses

Heat losses from the wellbore can cause condensation of steam and thereby increase the proportion of non-condensable gases. This effect is of most consequence at low flow rates where the velocity in the wellbore will permit the condensed fluid to drain under the influence of gravity. These conditions have been observed in steam wells flowing at so-called "bleeding" rates. For example, measurements of radon content in the discharge of one steam well at various times yielded Rn/Condensate ratios ranging from one to two orders of magnitude higher at bleeding rates (estimated at about 2,500 to 5,000 kg/hr (∿5,000 to ∿10,000 lb/hr) than were observed after several hours of performance tests (at rates of about 30,000 to 60,000 kg/hr (∿60,000 to ∿120,000 lb/hr).[5] In the same sets of samples CO_2/Condensate ratios were as much as three orders of magnitude higher and CH_4/Condensate ratios were as much as two orders of magnitude higher at bleeding rates compared to those observed after several hours at the performance test rates.[5]

Thus it is clear that, at least in the case of non-condensable gases, measurements made at flow rates where heat losses are proportionally large may not be representative of conditions at typical production rates.

In some situations it may be possible to make theoretical corrections for condensation due to heat losses. Relations developed for predicting and evaluating effects of heat losses during injection of hot fluids for oil recovery[9] can be modified to predict heat losses from geothermal wells.

3. Well Production History

The length of time a well has been produced can be an important parameter affecting the concentrations of some constituents observed in the discharge. Changes in some non-condensable gases to condensate ratios have been observed on both short and long time scales. During six pressure drawdown tests of steam wells measurements of Rn/Condensate ratios and CH_4/Condensate ratios in sequential samples fell into a repeated pattern.[5] An example of the data obtained from these tests is presented in Figure 7. Within about 1 hour after starting this test the values of the Rn/Condensate and CH_4/Condensate ratios dropped by about 1 order of magnitude from the values observed in bleeding rate samples taken just prior to test initiation. (This phenomenon has already been noted as due to the buildup of noncondensables in the wellbore at the low bleeding rate.) In the time interval between 1 hour and about 4 to 6 hours after starting the test, both ratios decreased by about 50%. After that, generally constant value of the Rn/Condensate ratio was observed through the end of the tests which lasted about 6 to 10 hours[5] and in one test which lasted 16 hours.[6] The data for CH_4/Condensate and Rn/CH_4 ratios showed more variability.

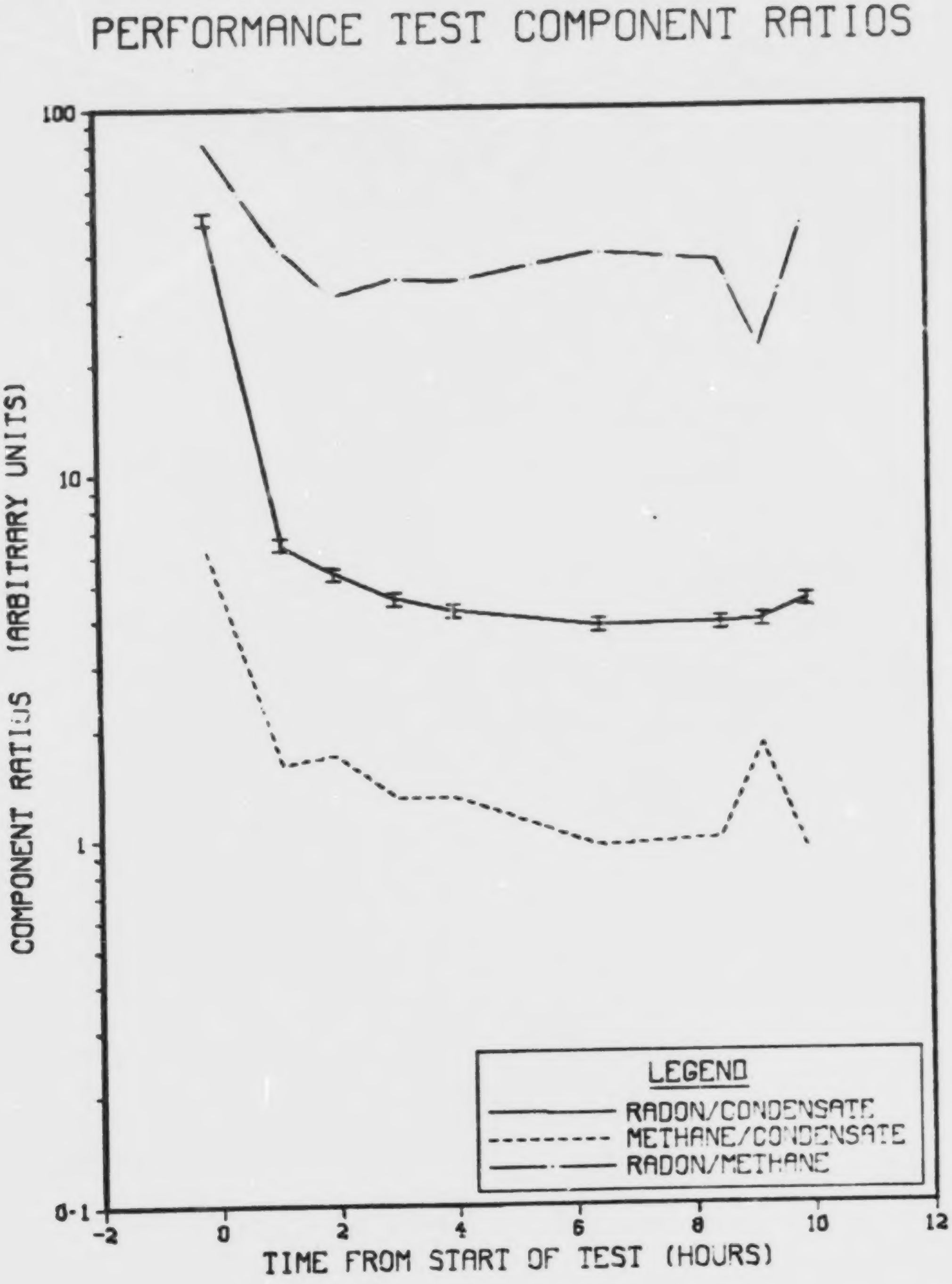

PERFORMANCE TEST COMPONENT RATIOS
COMPONENT RATIOS (ARBITRARY UNITS)
100
10
1
0·1
-2
0
2
4
6
8
10
12
TIME FROM START OF TEST (HOURS)
LEGEND
RADON/CONDENSATE
METHANE/CONDENSATE
RADON/METHANE

FIGURE 7

In addition to being fairly constant after about 4 hours, the Rn/Condensate ratios did not appear to depend significantly on the flowrate during the short-term drawdown tests. In one series of three drawdown tests where the maximum flowrate was 56% higher than the minimum, the average Rn/Condensate ratio at 4 or more hours varied by about 4%. In the second series, the maximum flowrate was about 10% higher than the minimum, but the average Rn/Condensate ratio at 4 or more hours varied by about 13%.[5] This contrasts with data on Rn/Condensate ratios observed over a period of many days, as shown in Figure 6, where there is an apparent dependence on flowrate. Figure 6 suggests that there may be a period of several days following a marked change in well flow rate before an approximate steady-state condition is achieved. In the case of radon, this may be partly due to the time required to establish radioactive equilibrium between the transporting fluid and the effective emanating power of the formation. For other non-condensable gases or dissolved constituents similar patterns may occur and it would seem necessary to investigate such possibilities carefully when planning sampling schedules.

On a longer time scale, Ellis[10] notes that the concentration of gas in steam from steam fields tends to decrease with time. At Wairakei, salinity as measured by chloride did not change more than 2% in 15 years. In systems of lower permeability concentrations are more variable.[10]

4. Corrosion Reactions

Barnes, et al.,[4] note that hydrogen released from water during the oxidation of well casings may constitute a large fraction of the total noncondensable gas in steam well discharges. They report hydrogen volume percents ranging from 50 to 73%. Such reactions occur at approximately constant rates and thus would contribute a much smaller proportion of H_2 to the noncondensables at higher flow rates.

Dissolved constituents could also be introduced by corrosion reactions and their significance would generally be expected to be related to flowrate. The importance of any contaminants is, in part, dependent on the types of analyses performed. It may be possible to analyze for the contaminant and make suitable corrections, as in the case of hydrogen. However, some other substances, such as iron, may react chemically and alter the sample irreversibly.

IV DOCUMENTATION OF HYDROLOGIC SYSTEMS RELATED TO GEOTHERMAL RESOURCES

Problems arise in identifying the presence and chemical characteristics of water overlying geothermal resources as most exploratory holes are drilled with fluids (water and/or mud) for cooling and cutting removal from the test hole.

Most, if not all, states require well or test hole construction to prevent the mixing of potable or fresh water by nonpotable or highly mineralized water penetrated by the hole. Thus it becomes necessary to initiate a testing program designed to evaluate the water resources at the site or use indirect methods of investigation to evaluate possible contamination of fresh water aquifers with highly mineralized fluids.

Indirect methods are generally employed due to lower costs. Careful collection of data can yield good results. A regional reconnaissance of the ground water is made by inventorying existing wells and springs that furnish water for domestic, municipal, industrial or agricultural use. In this way the depth, thickness, and chemical quality of the water bearing rocks are determined. This data can be extrapolated to the exploration site. Lithologic and geophysical logs of the test hole are necessary to confirm the extrapolated data.

Monitoring the chemical quality of the drilling fluids can aid in evaluating the penetration of an aquifer containing highly mineralized water. Preliminary field determinations are made with conductance cells and can be supplemented by laboratory analyses of selected constituents (e.g. SO_4, Cl, or TDS). The monitoring of increases or losses of the circulation fluids are also indicative of potential aquifers during drilling operations. Collection of water samples, though they may in part be contaminated by drilling fluids, can be obtained by packer tests, bailing during periods of lost circulation, or from the discharge line when air is employed as a cutting carrier.

At the LASL Dry Rock experiment, a regional reconnaissance was made of the surface and ground water and its chemical characteristics.[11] During drilling of GT-2, a fresh water aquifer occurred at depths of 125 to 137 m in volcanic rocks. In the underlying sediments, ten potential aquifers occurred between depths of 137 and 560 m, with a main zone of saturation occurring at depths of 560 to 730 m above the granite.

Interpretations were based on the results of the reconnaissance, lithologic and geophysical logs, and water samples collected and analyzed when circulation losses occurred or when air was substituted for water-mud as a circulation fluid. Monitoring of the quality of circulation fluids indicated a general increase in TDS and chlorides in the sediment section which was confirmed by the water samples collected. In the granite section, total uranium in the fluids increased from <1 to 60 μg/l. The sample of water from a fracture zone in the granitic rocks (identified from geophysical logs) collected during a packer test, contain a total uranium concentration of 125 μg/l.[12]

Thus, indirect methods can be used to estimate quality of water as well as hydrologic characteristics during drilling operation. This data is of value to determine well construction (casing schedules), to meet state criteria, and to establish a monitoring network for evaluating environmental effects of geothermal development.

V CONCLUSION

Many factors must be considered in the design and execution of a geothermal source sampling program and in the interpretation of the results. The composition of samples taken from a well may vary with factors such as heat losses in the well, the flowrate, the production history, and as a result of contamination introduced by corrosion reactions. All of these problems suggest that the most representative samples will be obtained when the well is operated at conditions close to those of actual production and after a long enough time to ensure that steady-state conditions have been reached for the constituents of interest.

The content of some materials encountered in geothermal fluids may fluctuate on both short and long time scales. The nature of such fluctuations must be understood for each situation in order to plan a sampling program with statistical validity.

Additional possibilities for variability and uncertainty related to sampling methods and sampling locations must be examined to preclude adverse effects on results. Where several alternative sampling techniques and analytical methods may be applied to measuring a given constituent, it would be desirable to have some intercomparison studies performed before adopting a standard or preferred method.

Geothermal source sampling must include techniques such as laboratory simulation in order to obtain predictive information for systems which do not contain natural fluids. Geothermal sampling programs must consider the need to document related hydrologic systems with some potential for connection to the geothermal resource.

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DRILL STEM TESTING AND SAMPLING OF GEO-PRESSURED BRINES

By

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Halliburton Services, Duncan, Oklahoma

ABSTRACT

Technology and equipment are available today for obtaining samples and reservoir data on geo-pressured and most geo-thermal wells. The ultra-deep search for hydrocarbons has fostered development of subsurface equipment capable of withstanding pressure differentials of 10,000 psi at 500° F. This equipment has been successfully used in a limited number of geo-thermal wells but has seen wide uses in the oil field. In addition to obtaining samples of the formation effluents, the following formation characteristics can be calculated: Static Reservoir Pressure, Indicated Flow Capacity, Transmissibility, Average Effective Permeability, Damage Ratio Theoretical Potential with Damage Removed, and the Approximate Radius of Investigation.

INTRODUCTION

Drill Stem Testing is a temporary completion of a well to gather data. As early as 1963, Drill Stem Testing (DST) equipment was being used to evaluate geo-thermal wells in the Salton Sea. On one of these open hole tests the bottom hole temperature was 450° F at 5000 feet. Sub-surface samplers were not available at that time; however, the desired data was gathered. The Key to this test and other deep hot tests was a new (in 1963) rubber compound for packer elements. Laboratory tested to 10,000 psi differential at 500° F this compound is standard today in oil field applications.

Many deep-hot-high pressure DST's have been run since 1963. Conditions in some instances have been extremely severe. Equipment and techniques used for these tests will be discussed.

EQUIPMENT

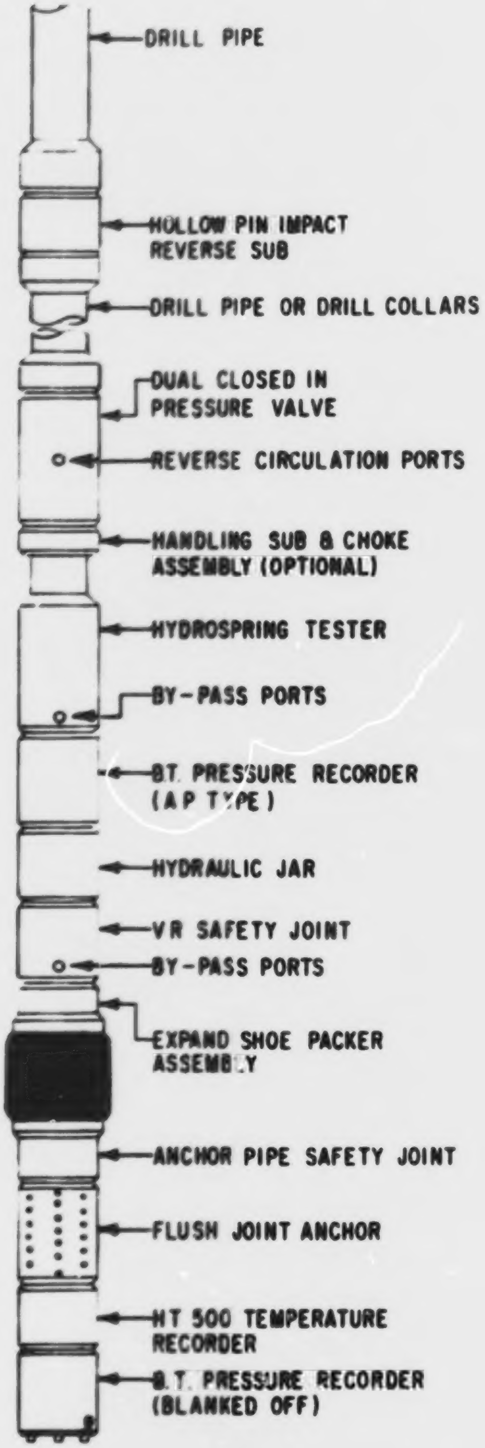
Four options are available today to those wishing to test and/or sample geo-pressured or geo-thermal reservoirs. Well conditions and the type data desired usually dictate the type equipment used.

Figure 1 illustrates a typical string of 'open-hole' tools used for Drill Stem Testing geo-pressured or geo-thermal wells in the open-hole (uncased hole). This is standard equipment for Drill Stem Testing in oil field applications. For geo-thermal wells where the Bottom Hole Temperature is expected to be in excess of 350° F, the tools are dressed with special high temperature seals and packer elements. Reference number one gives a detailed description of each item in this string.

Figure 2 shows the equipment schematically. Since the packer is larger in diameter than the other tools, a portion of the wellbore fluids enters the string through the anchor perforations and

FIGURE 1

OPEN HOLE SINGLE PACKER TEST


DRILL PIPE
HOLLOW PIN IMPACT REVERSE SUB
DRILL PIPE OR DRILL COLLARS
DUAL CLOSED IN PRESSURE VALVE
REVERSE CIRCULATION PORTS
HANDLING SUB & CHOKE ASSEMBLY (OPTIONAL)
HYDROSPRING TESTER
BY-PASS PORTS
BT PRESSURE RECORDER (AP TYPE)
HYDRAULIC JAR
VR SAFETY JOINT
BY-PASS PORTS
EXPAND SHOE PACKER ASSEMBLY
ANCHOR PIPE SAFETY JOINT
FLUSH JOINT ANCHOR
HT 500 TEMPERATURE RECORDER
B.T. PRESSURE RECORDER (BLANKED OFF)

FA

passes through the center of the packer. This fluid then exits through bypass ports in the VR Safety Joint and Hydro Spring Tester as shown in Figure 2-a.

While going in the hole, the Hydrospring's valve is closed so the drill pipe will be empty when it reaches bottom. When the testing string reaches the bottom of the hole, a portion of the drill pipe weight is applied to the string. This weight expands the packer element out against the wall of the hole, isolating the well bore fluids from the interval to be tested. As shown in Figure 2-b, this also closes the bypass ports; and after a brief time delay(normally 3-5 minutes), opens the valve in the Hydro-Spring Tester. The formation effluents then enter the test string through the perforations in the anchor pipe.

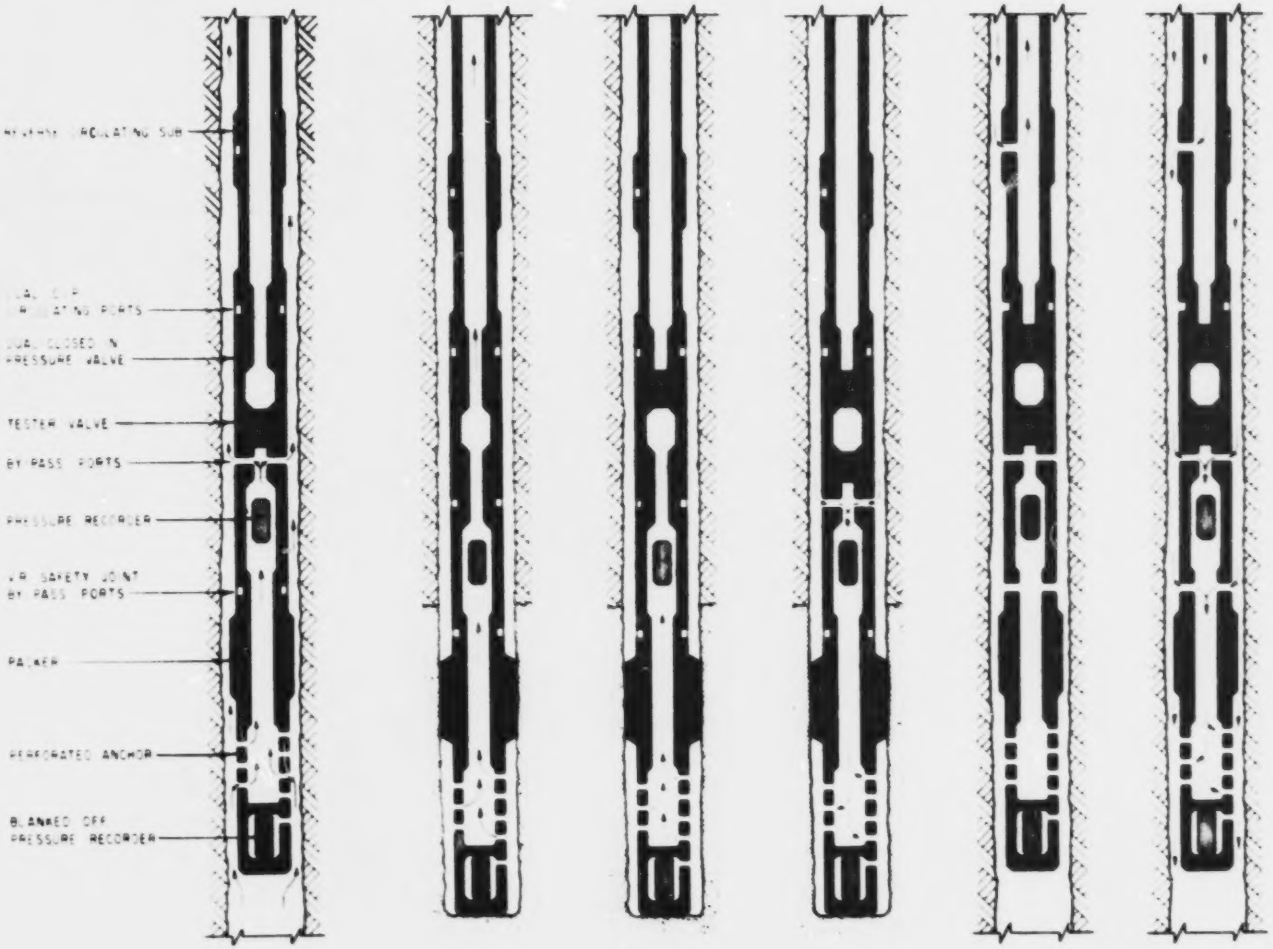
After the formation is flowed the desired length of time, clockwise rotation of the drill pipe closed the Dual CIP Valve, as shown in Figure 2-c, allowing the formation to repressure the area around the well bore.

When the formation has had time to develop a build-up pressure curve, the drill pipe is again rotated clock-wise. This moves the Dual CIP Valve to the second flow position, as shown in Figure 2-b.

Following the second flow period the drill pipe is rotated clockwise to close the Dual CIP Valve to develop another build-up curve. Figure 2-c illustrates this position.

FIGURE 2

FLUID PASSAGE DIAGRAM - OPEN HOLE DRILL STEM TEST


REVERSE CIRCULATING SUB
DUAL C.I.P. CIRCULATING PORTS
DUAL CLOSED IN PRESSURE VALVE
TESTER VALVE
BY PASS PORTS
PRESSURE RECORDER
V.R. SAFETY JOINT BY PASS PORTS
PACKER
PERFORATED ANCHOR
BLANKED OFF PRESSURE RECORDER

RUNNING IN (a)

FLOWING FORMATION (b)

FORMATION CLOSED IN (c)

EQUALIZING PRESSURE (d)

REVERSE CIRCULATING (e)

PULLING OUT (f)

FA

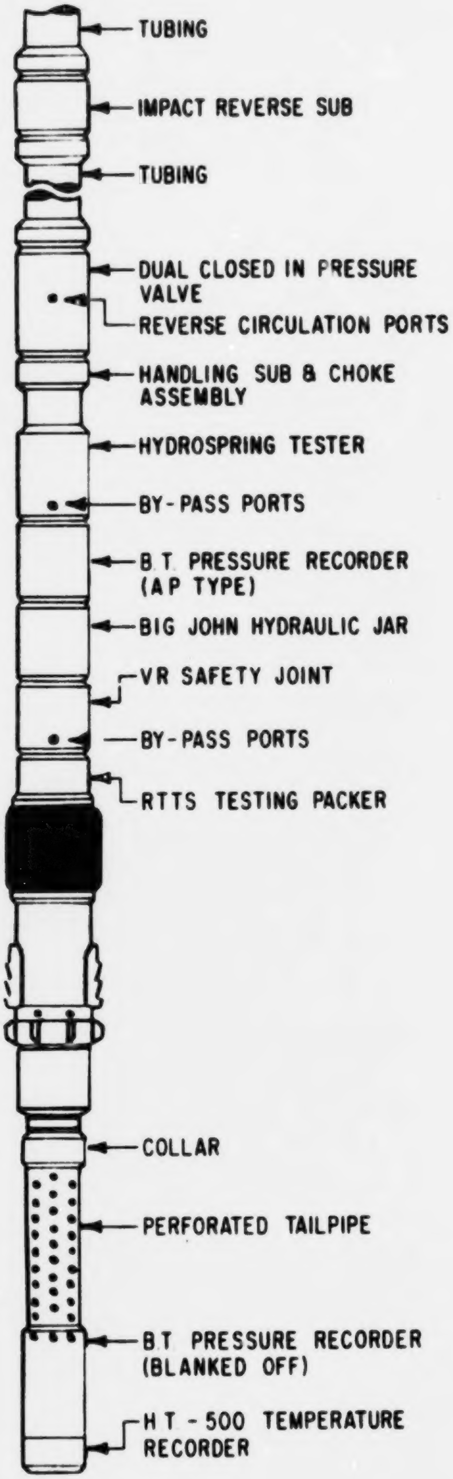
After the final closed-in-pressure period, the drill pipe is raised, closing the Hydrospring's Valve and opening the bypasses to equalize the pressure differential previously existing across the packer as shown in Figure 2-d. After a brief pause the pipe is raised further releasing the packer. A bar is then dropped through the drill pipe to open the Hollow Pin Impact Reversing Sub as shown in Figure 2-e. With the reversing valve, drilling fluid is then pumped down the annulus and back up the inside of the drill pipe to safely remove the formation effluents.

As shown in Figure 2-f, the reversing valve drains the drill pipe on the trip out of the hole. Fluid enters the bypass ports and exits through the Anchor Pipe perforations to bypass the packer.

When the formation is unconsolidated, or the hole has already been cased, a string of tools similar to those shown in Figure 3 are used for Drill Stem Testing a geo-thermal or geo-pressured reservoir. Tools from the VR Safety Joint upward are the same as those illustrated in Figure 2 for testing in the open hole. The prime difference when testing inside casing (commonly called a 'Hookwall Test') is the Packer.

The packer for Hookwall Testing is a casing packer having slips that grip the casing (when activated) to support the drill pipe weight necessary to expand the packer elements and operate

FIGURE 3 - HOOK WALL PACKER TEST


TUBING
IMPACT REVERSE SUB
TUBING
DUAL CLOSED IN PRESSURE VALVE
REVERSE CIRCULATION PORTS
HANDLING SUB & CHOKE ASSEMBLY
HYDROSPRING TESTER
BY-PASS PORTS
B.T. PRESSURE RECORDER (A.P. TYPE)
BIG JOHN HYDRAULIC JAR
VR SAFETY JOINT
BY-PASS PORTS
RTTS TESTING PACKER
COLLAR
PERFORATED TAILPIPE
B.T. PRESSURE RECORDER (BLANKED OFF)
H.T. - 500 TEMPERATURE RECORDER

FA

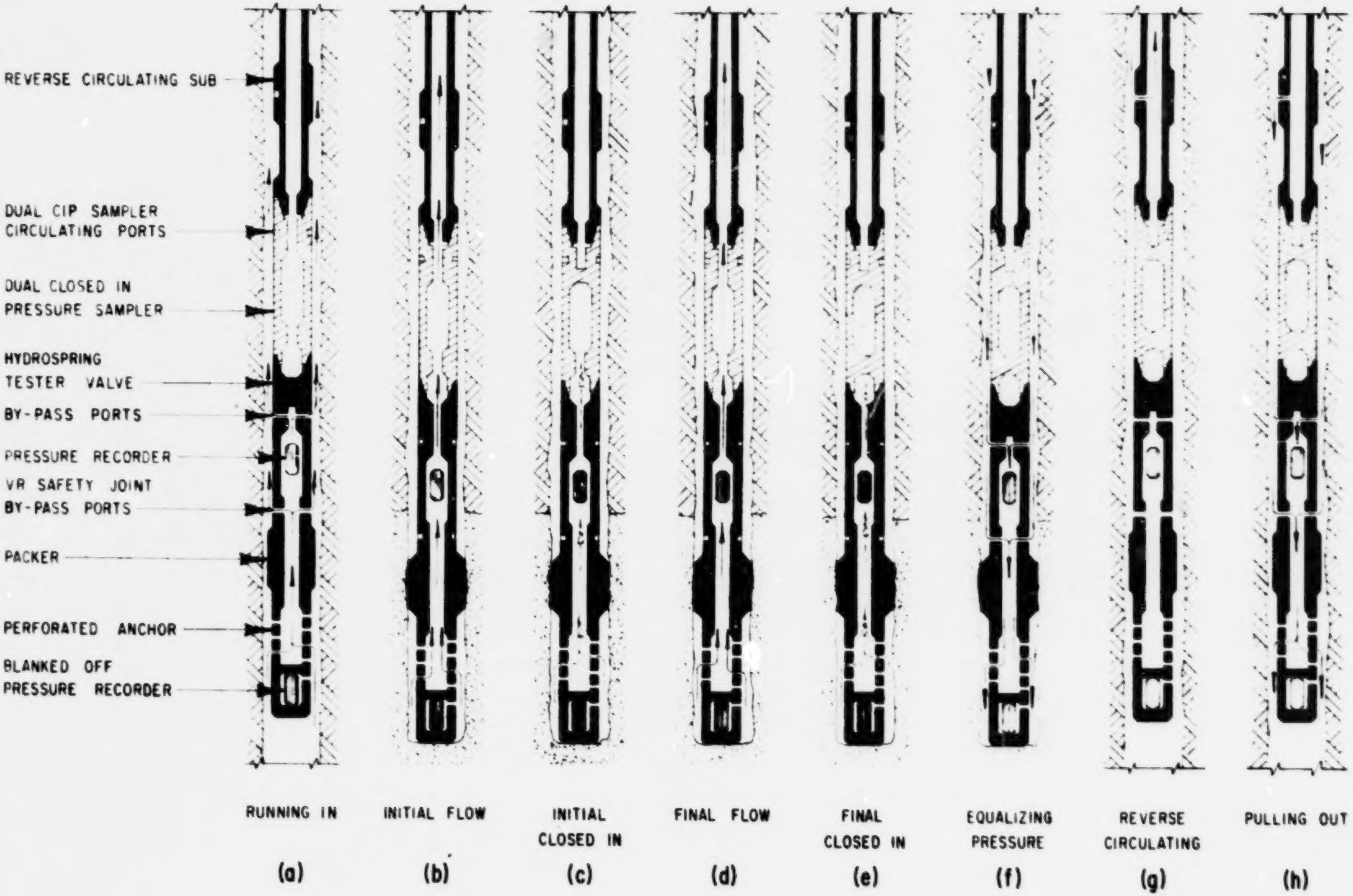
the other tools. With the casing packer the slips make it unnecessary to set the string on bottom. Operating sequence is similar to that described above for an open hole test.

Effluent samples can be trapped down hole at final flow pressure and returned to the surface for analysis. This analysis can either be done at the wellsite (in oil field applications) or the tool can be taken to the laboratory for a more exacting analysis. The sample chamber is simply attached to the lower end of the Dual CIP Valve and is operated by the Dual CIP Valve. As shown schematically in Figure 4, the sample is trapped when the Dual CIP is rotated to the final closed-in-pressure position.

A new tool has opened up two new types of formation evaluation, a Limited Entry Type Open Hole Test and a Limited Entry Type Hookwall Test. Operationally the two types of tests are similar. Equipment wise the only difference is in the type packer used.

The Limited Entry Type Test was developed as a sampling technique for deep, hot, hydrogen-sulfide environments.[2,3] Considerable time was spent in seeking special seals for this hostile environment.[4] Design criteria for this tool was to sample hydrogen sulfide reservoirs where the bottom hole pressure could be as high as 24,000 psi and the bottom hole temperature might be 450° F. To meet these specifications the system shown in Figure 5 was developed.

FIGURE 4 - OPERATIONAL DIAGRAM - DUAL CIP SAMPLER


REVERSE CIRCULATING SUB
DUAL CIP SAMPLER CIRCULATING PORTS
DUAL CLOSED IN PRESSURE SAMPLER
HYDROSPRING TESTER VALVE
BY-PASS PORTS
PRESSURE RECORDER
VR SAFETY JOINT BY-PASS PORTS
PACKER
PERFORATED ANCHOR
BLANKED OFF PRESSURE RECORDER

RUNNING IN (a)
INITIAL FLOW (b)
INITIAL CLOSED IN (c)
FINAL FLOW (d)
FINAL CLOSED IN (e)
EQUALIZING PRESSURE (f)
REVERSE CIRCULATING (g)
PULLING OUT (h)

FA

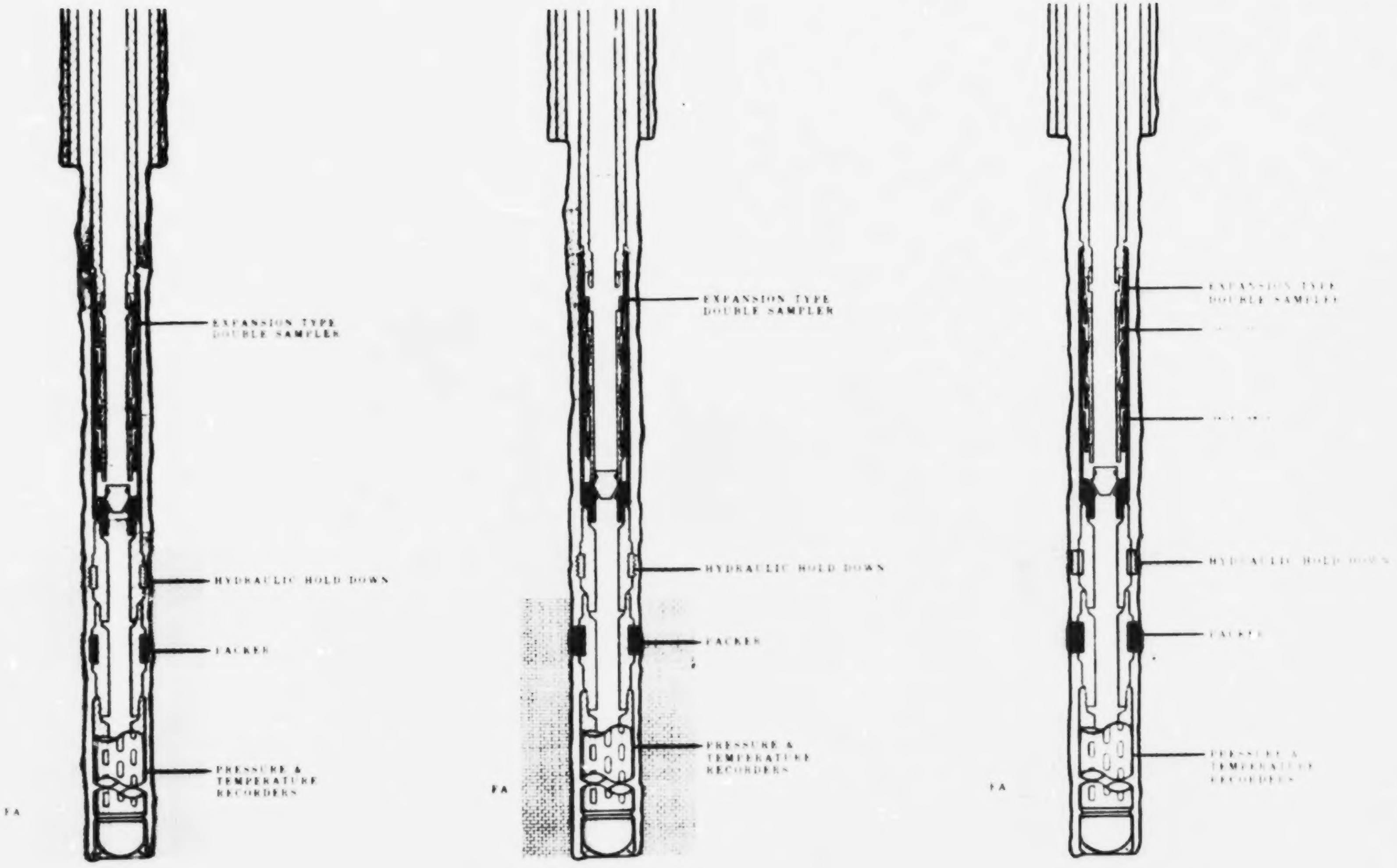
To date this equipment has been used on two tests, one offshore and one inland. These tests indicated that this is an operational system.

For testing geo-thermal or geo-pressured reservoirs, all tools, except the Expansion Type Double Sampler, will be standard tools dressed for high temperature applications.

Key to the limited entry sampling technique is the new Expansion Type Double Sampler. This tool is capable of trapping two bottom hole samples and bringing them back to the surface for analysis. The sample chambers expand as the tool is brought out of the hole in order to reduce the sample pressures for safer handling at the surface. Expansion of the chambers, plus the reduction in pressure due to the temperature change, normally provides a surface pressure in the chambers equal to 40 to 60% of bottom hole pressure. Figure 5 is a schematic of the Expansion Type Double Sampler. The tool is open so that the drill pipe fills with drilling fluid as the tools are run in the hole. A description of a typical operating sequence describes the other advantages of the system.

Since the tool string is open ended, the drill pipe fills with well bore fluid as the tools are run in the hole. Once on bottom, prior to setting the packer, the drill pipe is partially displaced with a light fluid such as water or diesel, as shown in Figure 5-a. The amount of water or diesel placed in the drill pipe is just

FIGURE 5


EXPANSION TYPE DOUBLE SAMPLER
HYDRAULIC HOLD DOWN
PACKER
PRESSURE & TEMPERATURE RECORDERS
FA
EXPANSION TYPE DOUBLE SAMPLER
HYDRAULIC HOLD DOWN
PACKER
PRESSURE & TEMPERATURE RECORDERS
FA
EXPANSION TYPE DOUBLE SAMPLER
HYDRAULIC HOLD DOWN
PACKER
PRESSURE & TEMPERATURE RECORDERS
FA

(A)
DISPLACING TUBING

(B)
PRODUCING FORMATION

(C)
PUMPING RECOVERY
BACK INTO FORMATION

enough to clean out the rat hole (below the packer) and get the formation material up to the sampler. If the formation pressure is low, it may be necessary to put a greater amount of cushion in the drill pipe to further reduce the hydrostatic head. Normally 10 to 20 barrels of cushion is adequate. With the cushion in the drill pipe the packer is set. The weight applied to the packer activates the hydraulic time delay in the Sampler. After a brief time delay, the Sampler closes off the inside of the tool and opens the two sample chambers so that all the flow passes through the chambers. The surface equipment valves can then be opened and the cushion slowly flowed out of the drill pipe as shown in Figure 5-b. The cushion is directed to a measuring tank so that the amount of formation material entering the system is carefully controlled. When all the cushion has been recovered, the surface equipment valve is closed and the drill pipe is raised to the free point to close the sample chambers. Raising the drill pipe automatically moves an 'Indexing J' within the tool to the next position so that the drill pipe weight can be placed back on the packer while the sample chambers remain closed. With the sample chambers closed, the center of the tool is open as shown in Figure 5-c. While the surface equipment is closed, a closed-in-pressure can be taken to obtain additional reservoir data. With the special hydraulic hold down packer the formation fluids can be pumped back into the formation. If the formation material cannot be pumped back into the formation, the packer can be unseated and the recovery reversed out. As the tools are withdrawn from the hole, the sample chambers expand, reducing the pressure inside to approximately 40-60% of bottom hole pressure. These expanded sample chambers can then be separated from the tool string and one drained on location. This gives a quick preliminary idea of the type materials present in the formation while the other sample is being transported to the laboratory for a more thorough analysis.

The Expanding Type Double Sampler permits the operator to use the limited entry type technique to obtain samples of the formation material early in the program. In hardrock formations this technique can be used to determine if standard material liners can be used, or if exotic liners will be required because of hydrogen sulfide. In unconsolidated formations, the tool allows the operator to obtain samples of the formation materials so he can determine if special tubing will be required because of hydrogen sulfide or if it will be safe to test with the drill pipe.

TEST PROCEDURE

The Key to obtaining maximum data from the Drill Stem Test is the procedure. Each test will react differently due to previous activity during the drilling operation, formation characteristics,etc. Because of these differences, 'cook-book' test procedures are not practical. The length of the flow and closed-in-pressure periods should be selected at the well site, based on surface reactions of the well during the test. As a general rule-of-thumb, low permeability formations require longer flow and closed-in-pressure times than high permeability formations.[5] In either case, the flow periods must be long enough for the well to clean up and to draw the reservoir down. The first flow period must be long enough to remove the 'super-charge' so that meaningful data can be collected.[6] Wells that flow to the surface should be flowed long enough to reach a semi-steady flow rate and that rate should be measured. If reservoir data is desired from wells that do not flow to the surface, the well should not be permitted to die; i.e., it should not be flowed until the back pressure created by the hydrostatic head is approaching reservoir pressure. Surface indications of a well killing itself is obvious in the bubble bucket.

On deep Drill Stem Tests it is sometimes necessary to put a light fluid(commonly called a cushion), such as fresh water or diesel oil, in the drill pipe to help protect the drill pipe against the collapse pressure created by the drilling fluid in the annulus. These cushions can offer both advantages and disadvantages depending on the type formation being evaluated.

On high permeability wells capable of producing at high rates, a full cushion helps provide better well control, assuming the formation pressure is adequate to overcome the hydrostatic head of the cushion. When testing very hot formations where salt water is used as the drilling fluid, cushions can provide a back pressure to help prevent flash separation of the drilling fluid (rat-hole fluid) as it passes through the reduced diameters of the tools. Should this flash separation occur, the precipitants could plug the tools aborting the test. Where a cushion is not required to protect the drill pipe, but flash separation is a possibility, a gas cushion can be used. The gas cushion, usually nitrogen, can be slowly bled-off at the surface permitting formations not capable of producing against a liquid cushion to flow.

When testing unconsolidated formations a cushion is beneficial as it will create a back pressure on the formation the instant the Hydrospring opens. With out the back pressure, the face of these formations tend to 'explode', when the well bore pressure is reduced as the Hydrospring opens, plugging the tools and sometimes the hole.

Low permeability formation tests, on the other hand, are usually hindered by cushions. This type formation normally requires longer flow and closed-in-pressure periods. The additional back pressure of the cushion will require even more time to clean up the well and sufficiently draw the reservoir down.

CONCLUSIONS

Equipment and technology are available today to Drill Stem

Test and sample most geo-pressured and geo-thermal wells. Proper testing procedures and techniques will gather the data to make an evaluation of the economic feasibility of a well.

Preplanning of the test should include adequate lead time for the service contractor to obtain the special high temperature seals and packer elements. These items are not normally stocked so that they will be fresh for each application.

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THE SALINITY PROFILE OF THE EAST MESA FIELD AS DETERMINED FROM DUAL INDUCTION RESISTIVITY AND SP LOGS

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U.S. Bureau of Reclamation
Boulder City, Nevada
October 1975

In a water dominated geothermal reservoir such as the East Mesa Field or, if you prefer, a high temperature ground-water reservoir, it is practical to obtain the general dimensions of dissolved mineral concentration by interpretation of dual induction resistivity logs and self-potential logs. Values so obtained may be substantially greater or less than those obtained by laboratory analyses of water samples from the same zones. Therefore, it is necessary to establish calibrating coefficients by borehole sampling and laboratory analyses.

In the East Mesa Field, a useful method of obtaining representative fluid samples is by drill stem testing during drilling. The saturated sand beds as deep as 7,500 feet in the East Mesa Geothermal Reservoir produce readily under drill stem testing. In a 35-minute period, we may obtain a column of water that extends to within a few hundred feet of land surface; in fact, we would flow water at the surface on most drill stem tests but for blocking the tool with sand. We obtain a good flush of the sand formation tested as indicated by the bottom hole temperature obtained by maximum recording thermometers run with the drill stem testing tool. The temperature we obtain is very near equilibrium and invasion has been overcome. Determination of the temperature profile several weeks after completion of wells shows that near equilibrium conditions were reached during the drill stem test by the production of formation fluid.

Our procedure for deriving salinities from logs is as follows: We first make a lithologic interpretation using the natural gamma ray log, the SP log, and the resistivity log (see Figure 1). Using these three logs, we are able to pick the tops and bottoms of individual sand beds with confidence. The next step is to draw the clay or clay-shale line on the SP log. Then we draw a sandline wherein we give greater weight to the thick sand bed deflections than to the thin sand bed deflections. We then read a value of static SP deflection for each sand bed which is the difference between the clay-shale baseline and the sandline in millivolts. Next we pick resistivity values in OHM-meters for each permeable bed, which is sand or sandstone in the geologic environment of East Mesa. Our methodology is to pick a shallow resistivity value and a deep resistivity value. In picking these values, we give considerable weight to that portion of the curve which suggests the most permeable part of the sand. Our shallow reading presents the flushed zone and our deep reading represents the unflushed zone. Values of SP and resistivity obtained are inserted in formulae described in logging company manuals.

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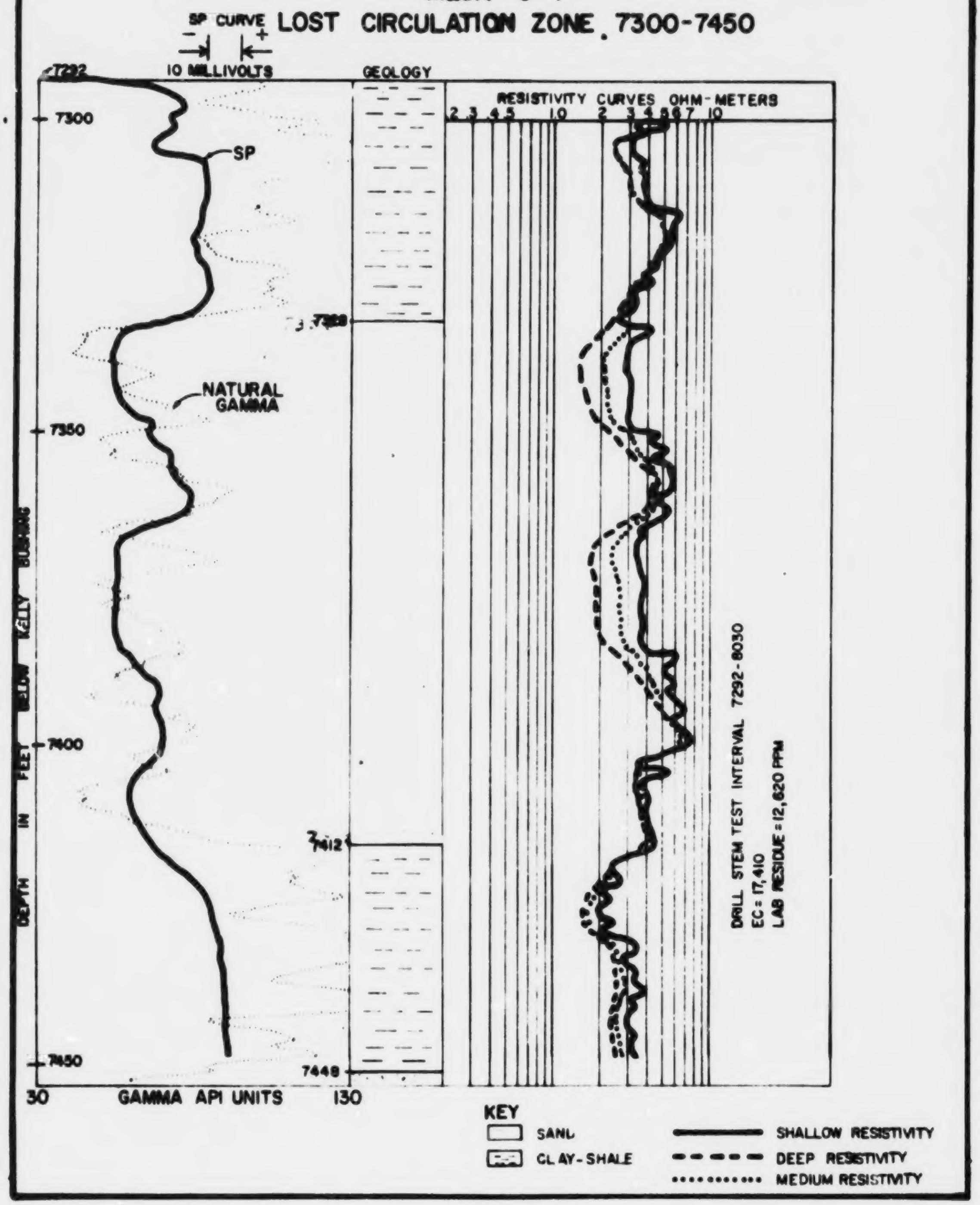
Figure 1

GEOTHERMAL TEST WELL
MESA 6-1
LOST CIRCULATION ZONE 7300-7450



The results of our computations of total salinity on the logs of two shallow wells, one in the Yuma Valley and one at the East Mesa Geothermal Station, are shown in Figures 2 and 3. The well in Yuma Valley was drilled to test foundation conditions for a desalting plant site. The logs depicted on the slide include a geologist's log based upon drilling character and an SP curve and two resistivity curves. This well is screened from 50 to 85 feet and was pump tested and water samples were obtained. Electrical conductivity of the sampled interval according to laboratory analysis is 2,270 p/m, according to the SP curve is 3,660 p/m, and according to the two resistivity curves is 2,000 p/m.

An SP log of a water supply well at the geothermal site on East Mesa indicates a high mineral concentration in sand at the water table and a sharp decrease in concentration in the thin sand bed below the first thick clay bed (Figure 3). The higher salinity in the first sand is indicated by the stronger SP deflection in the first sand than in the second sand. Pumped water from two shallow sand-point observation wells nearby, one completed in the upper sand and the second completed in the lower sand, confirm what the SP log indicated even though the values computed by the conventional formula differ substantially from the laboratory values. In order to obtain a perfect match, it would be necessary to account for all the factors that influence the SP curve including differences in the basic chemical makeup of the formation water and the drilling mud filtrate and stray electrical currents emanating from forces outside the borehole.

A general trend of the salinity profile throughout some 8,000 feet of strata is computed from the dual induction logs and SP logs of geothermal Well Mesa 6-1 (see Figure 4). Both the self-potential and resistivity curves show broad zonations through the interval measured. The resistivity curve shows mineralization of less than 5,000 p/m down to a depth of 1,450 feet. From 1,450 feet to 6,100 feet ± is 5,000 to 6,000 p/m generally but locally approaching 9,000 p/m.

Four drill stem tests were made during the drilling of Mesa 6-1.

Laboratory analyses of fluid samples obtained indicated the following total dissolved solids: 7,620 p/m from 2,505 to 2,601 feet depth; 5,720 p/m in the interval 4,445 to 4,480 feet; 1,850 p/m from 5,557 to 5,607 feet depth; and 1[illegible],620 p/m from 7,292 to 8,030 feet depth. With respect to the latter interval, we have considerable evidence that most of the fluid probably came from the lost circulation zone between 7,300 and 7,400 feet depth. Below 7,300 feet we cannot corroborate our methods and computations with drill stem test data.

We have no airtight explanation for the reversal of the curves but are disposed to state that there was such heavy mud loss that neither the resistivity nor the SP curves sensed the in situ formation water. The geologic terrane penetrated apparently has fracture permeability which permits deep mud invasion. Drilling below 7,100 feet, the hole took mud continuously. Large quantities were lost between 7,300 and 7,400 feet requiring the setting of a cement plug to regain circulation so that we could continue

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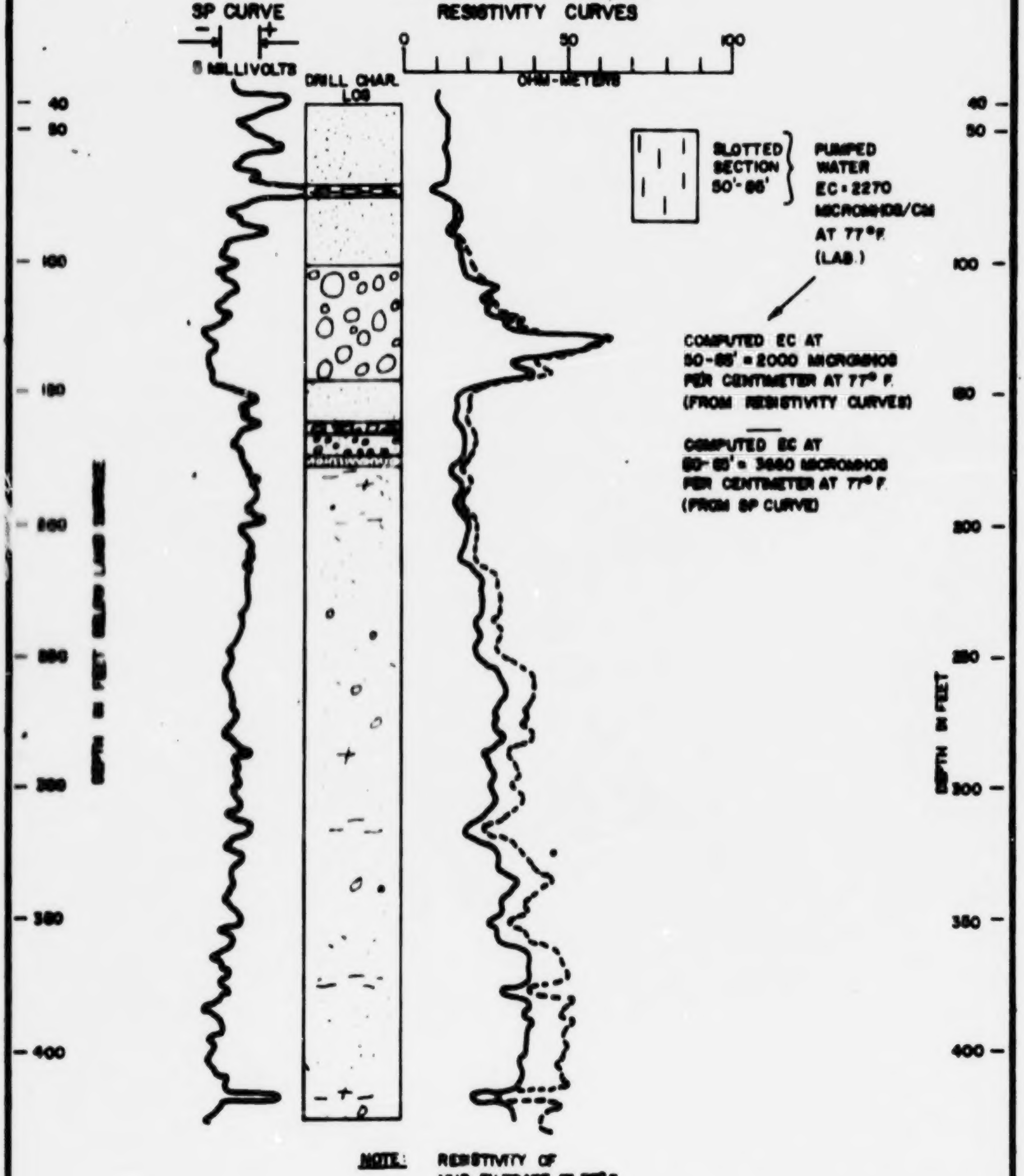
Figure 2

YUCCA DESALTING PLANT SITE
YUMA, ARIZONA
PR-12 Y TEST HOLE



SLOTTED SECTION 50'-66'

PUMPED WATER
EC = 2270
MICROMHOS/CM
AT 77°F.
(LAB.)

COMPUTED EC AT
50-66' = 2000 MICROMHOS
PER CENTIMETER AT 77° F.
(FROM RESISTIVITY CURVES)

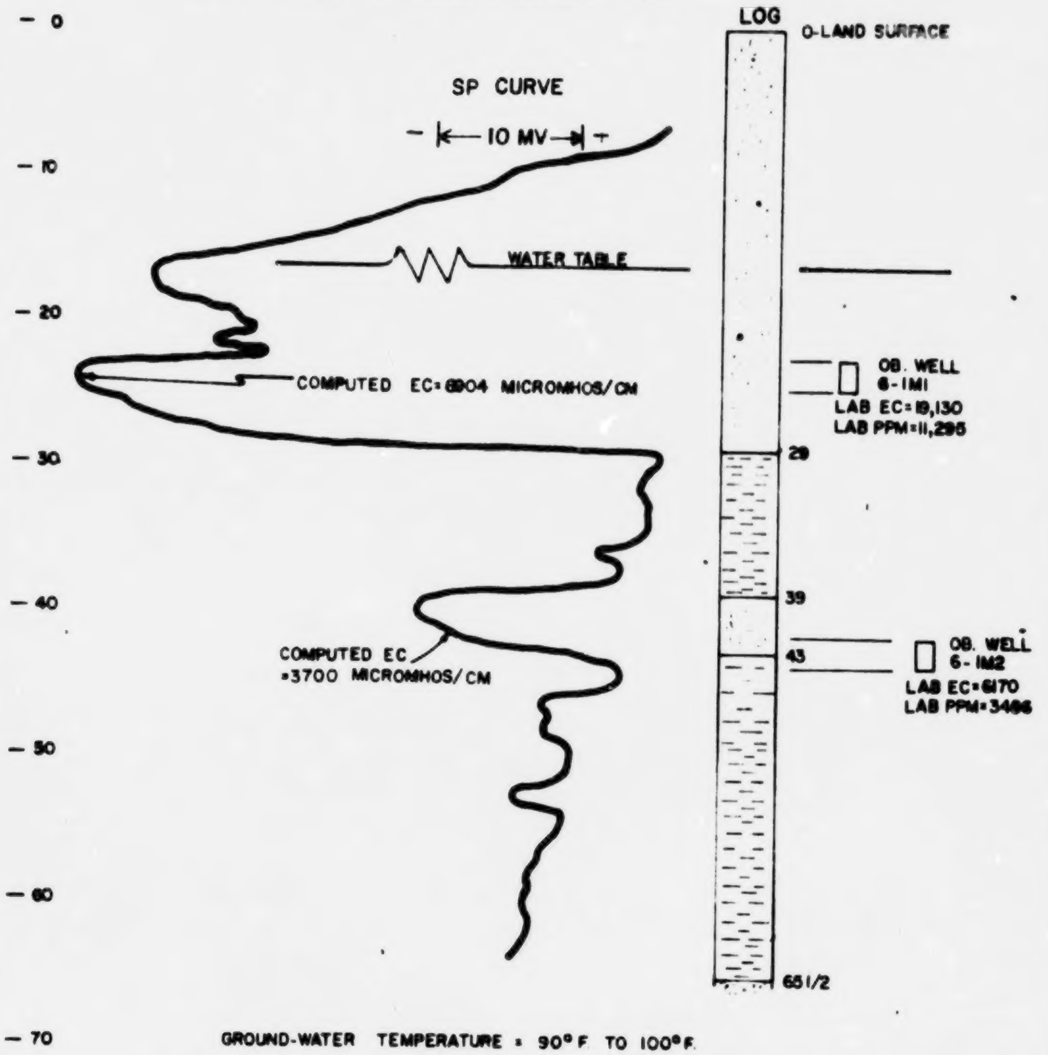
COMPUTED EC AT
50-66' = 3660 MICROMHOS
PER CENTIMETER AT 77° F.
(FROM SP CURVE)

NOTE: RESISTIVITY OF
MUD FILTRATE AT 77° F.
= 4.44 OHM-METERS

Figure 3

WATER SUPPLY WELL 6-1S2
EAST MESA GEOTHERMAL WELL SITE

SP LOG WATER QUALITIES COMPARED TO PUMPED WATER QUALITIES
FROM OBSERVATION WELLS 6-1M1 AND 6-1M2

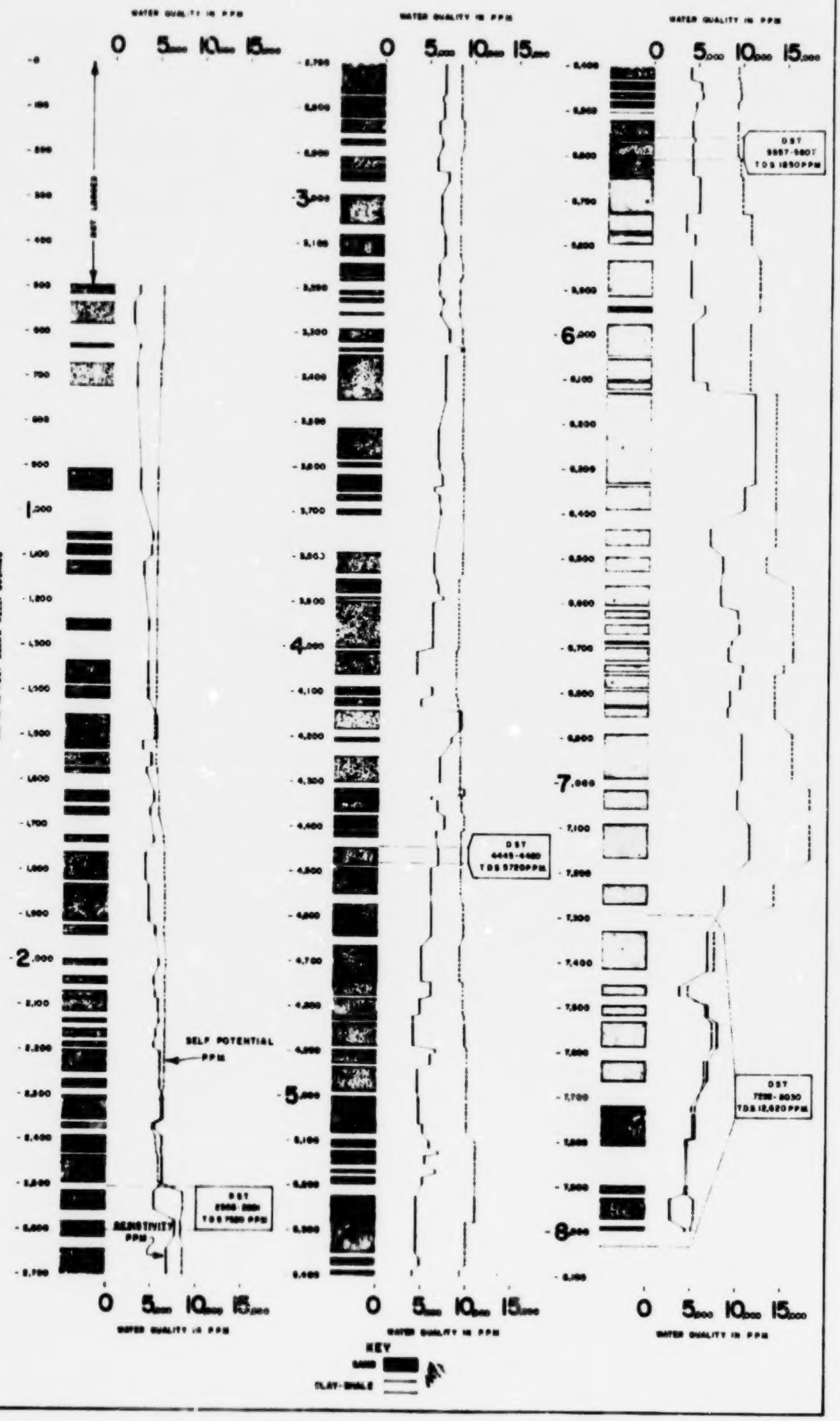


GROUND-WATER TEMPERATURE = 90° F TO 100° F

NOTE: Although the computed qualities differ considerably from the pumped laboratory analyzed qualities, the comparative differences between the two zones are apparent. That is, the upper zone is indicated by the SP log to be considerably more saline than the lower zone, which is confirmed by the laboratory analyses.

Figure 4

WATER QUALITY PROFILE
MESA 6-1



drilling to the target depth of 8,000 feet. We ended up with fresh mud not only in the borehole but also with a substantial quantity in the fractured terrane. We are unable to place much confidence in the values computed below 7,300 feet for two reasons. One, the value of the mud filtrate resistivity used for the calculation may not be correct; and, two, deep mud invasion of the fractured terrane may have biased the computations. The computed salinities may reflect a mud-soaked formation rather than the saline character of the natural water that was indicated by the drill stem test.

With respect to the low salinity of 1,850 p/m in the interval 5,557 to 5,607 feet, we computed a total salinity of about 4,000 p/m from the resistivity curves of the dual induction log. We have no satisfactory explanation for this difference.

We have also computed the salinity profile throughout about 6,200 feet of strata in Mesa 31-1 which was drilled in the cooler part of the East Mesa geothermal field (see Figure 5). The two salinity curves computed from the resistivity and self-potential logs more or less parallel each other as was the case in Mesa 6-1. Also, the resistivity values computed are lower than the self-potential values and more nearly fit actual formation conditions based upon our meager data from drill stem tests. The match between the drill stem test and results computed from the resistivity curves of the dual induction log are good. Laboratory analyses of water from drill stem test interval at depth 4,333 to 4,395 feet gave a total dissolved solids ranging from 2,000 to 2,500 p/m. We computed 2,000 p/m from the resistivity curves. In the drill stem test interval 5,656-5,696 feet, not shown on Figure 5, laboratory analyses of samples gave total dissolved solids ranging from about 1,900 to about 2,220 p/m. We computed about 1,300 p/m from the resistivity curves. The levels of mineral concentration in the water throughout the reservoir profile are substantially less at Mesa 31-1 than at Mesa 6-1.

A comparison of salinity profiles as computed from geophysical logs of three East Mesa geothermal wells shows a common pattern (see Figures 7, 8, and 9). To a depth of 6,000 feet, three salinity zones seem recognizable. Little information is available above 1,000 feet. Zone 1 is from 1,000 to about 2,000 feet in which salinities of 2,000-3,000 p/m seem to prevail. Zone 2 is an irregular zone from 2,000 to about 4,000 feet in which salinities of 2,000-5,000 p/m seem to occur. Zone 3 is from 4,000 to 6,000 feet in which water of about 2,000 p/m prevails. Mesa 6-1 (Figure 4) seems to indicate a fourth zone beginning shortly below 6,000 feet in which water in the 10,000 p/m range occurs, although there is confusion about the water salinity below 7,300 feet. A comparison of the Bureau of Reclamation wells with apparent salinity profiles of other deep wells in the area but outside the East Mesa Anomaly suggests similar zonations in the water quality profile.

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Figure 5

WATER QUALITY PROFILE

MESA 31-1

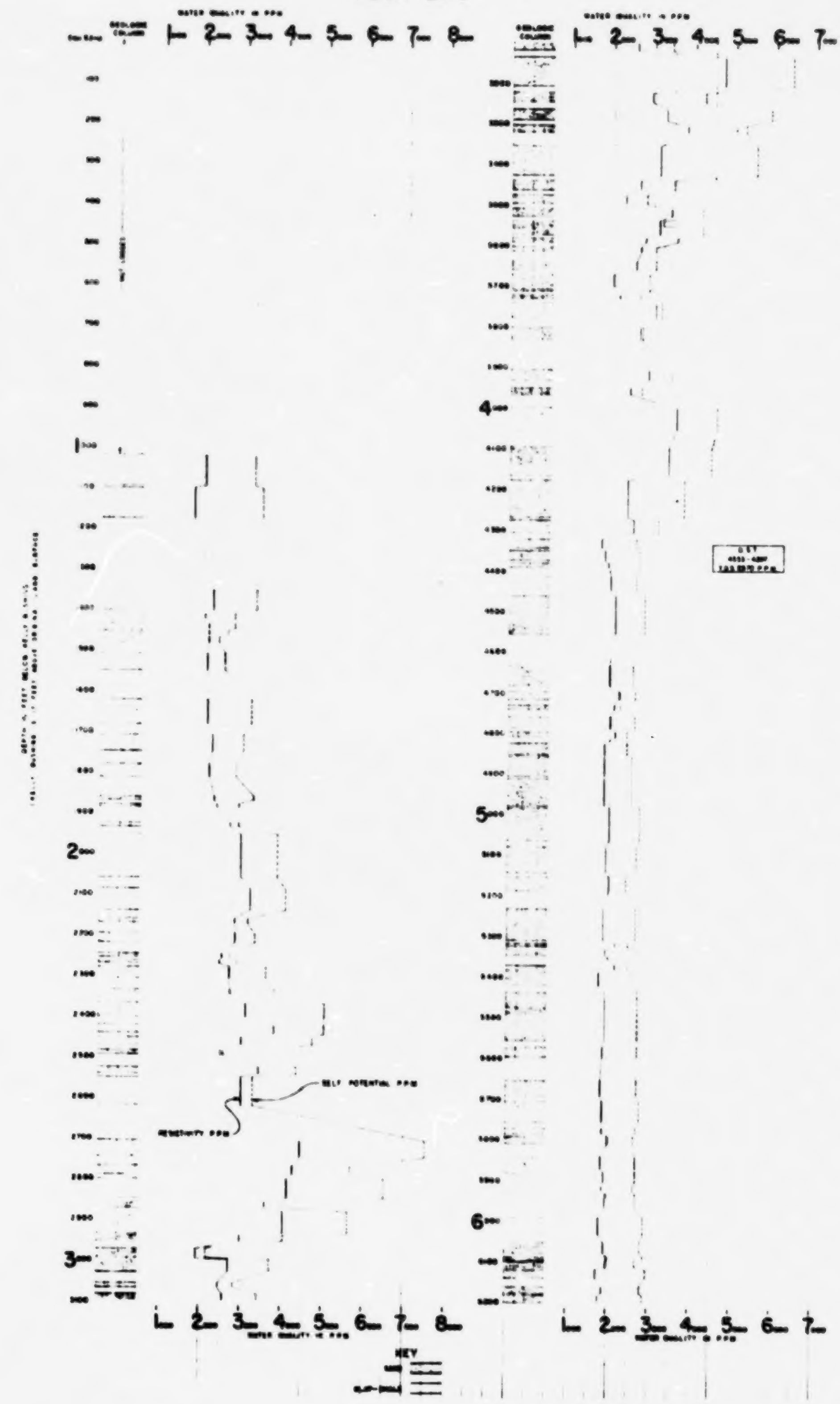
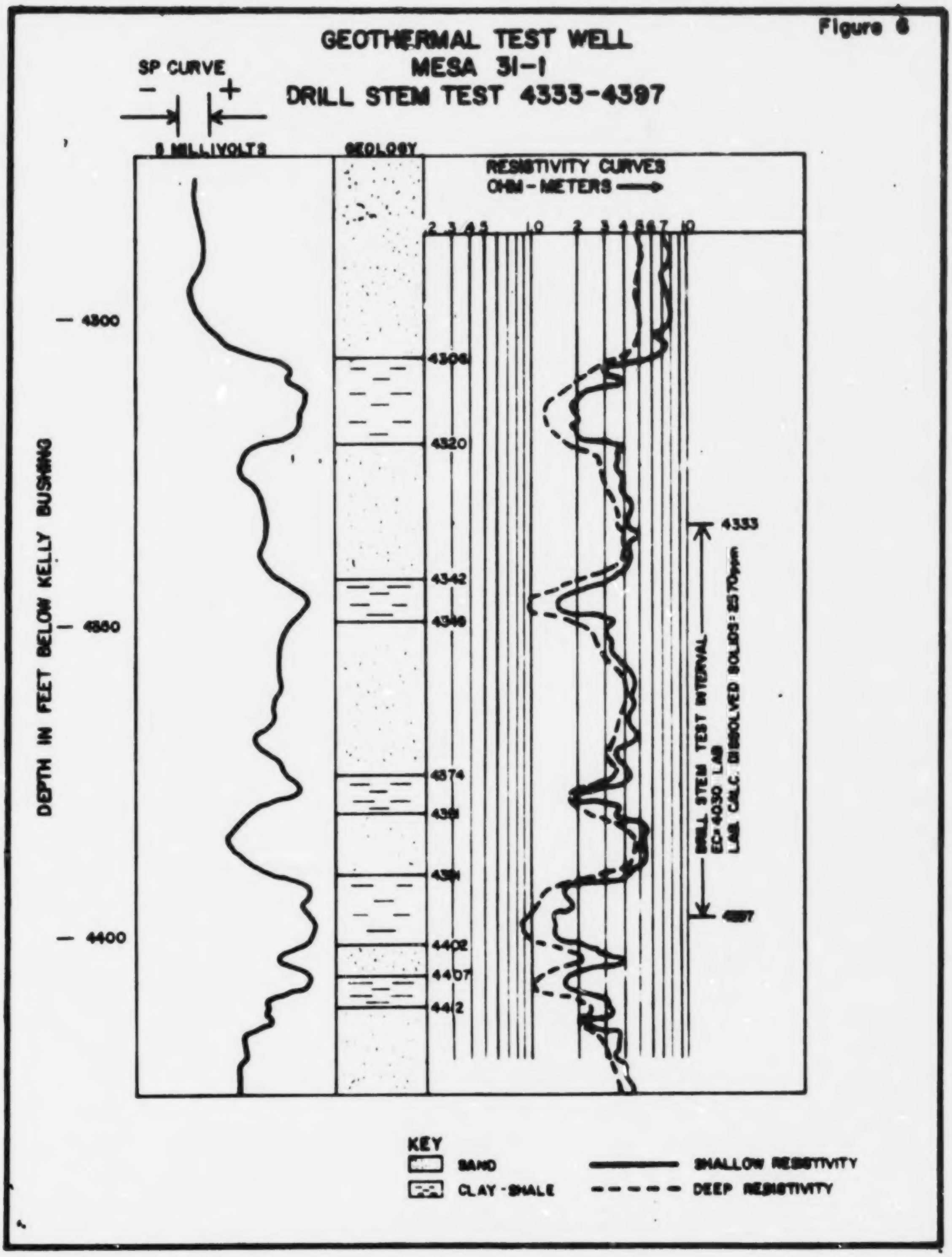


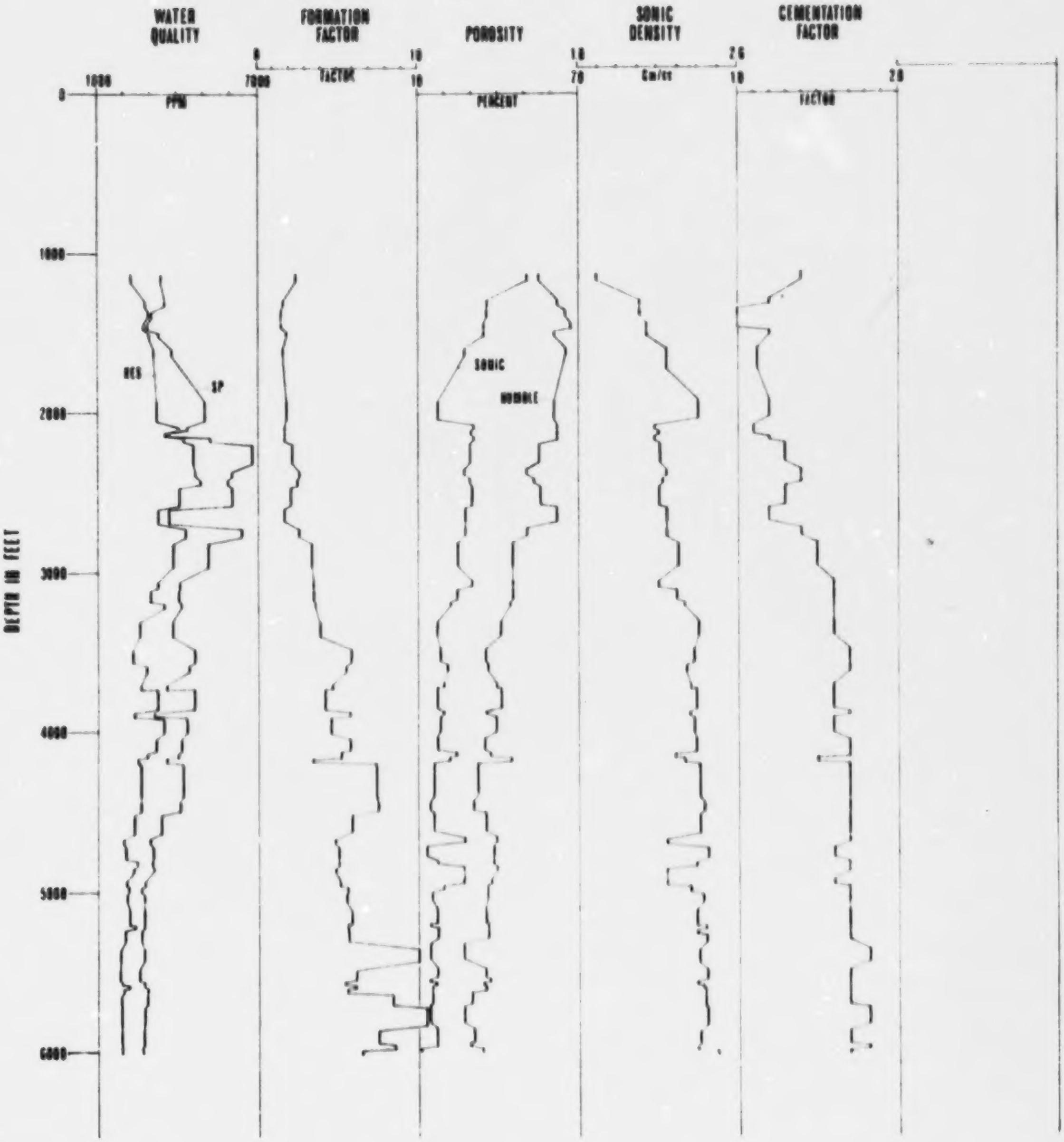
Figure 6

GEOTHERMAL TEST WELL
MESA 31-1
DRILL STEM TEST 4333-4397



COMPUTED CURVES OF LOG MESA 5-1

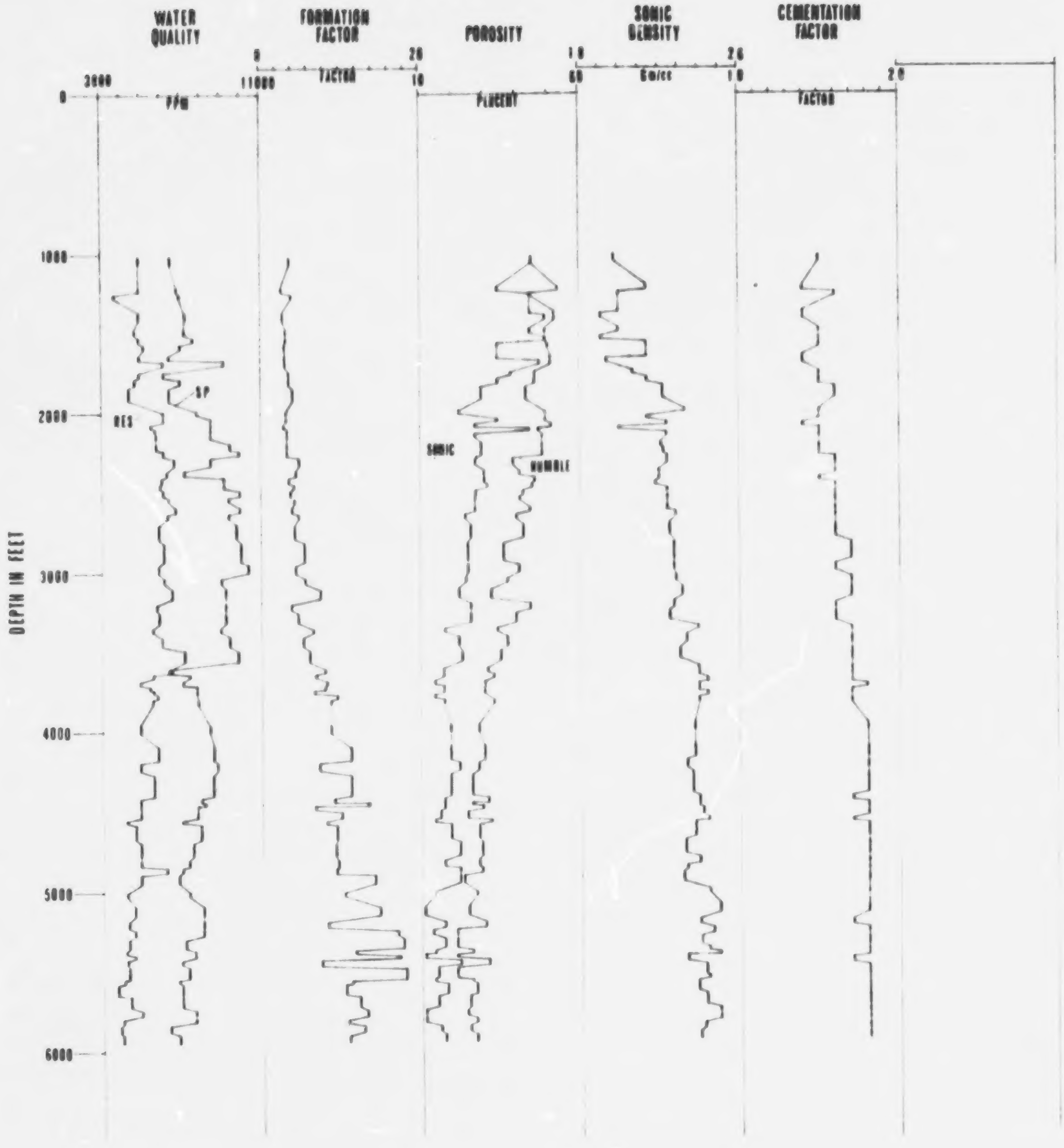
Figure 7



COMPUTED CURVES OF LOG

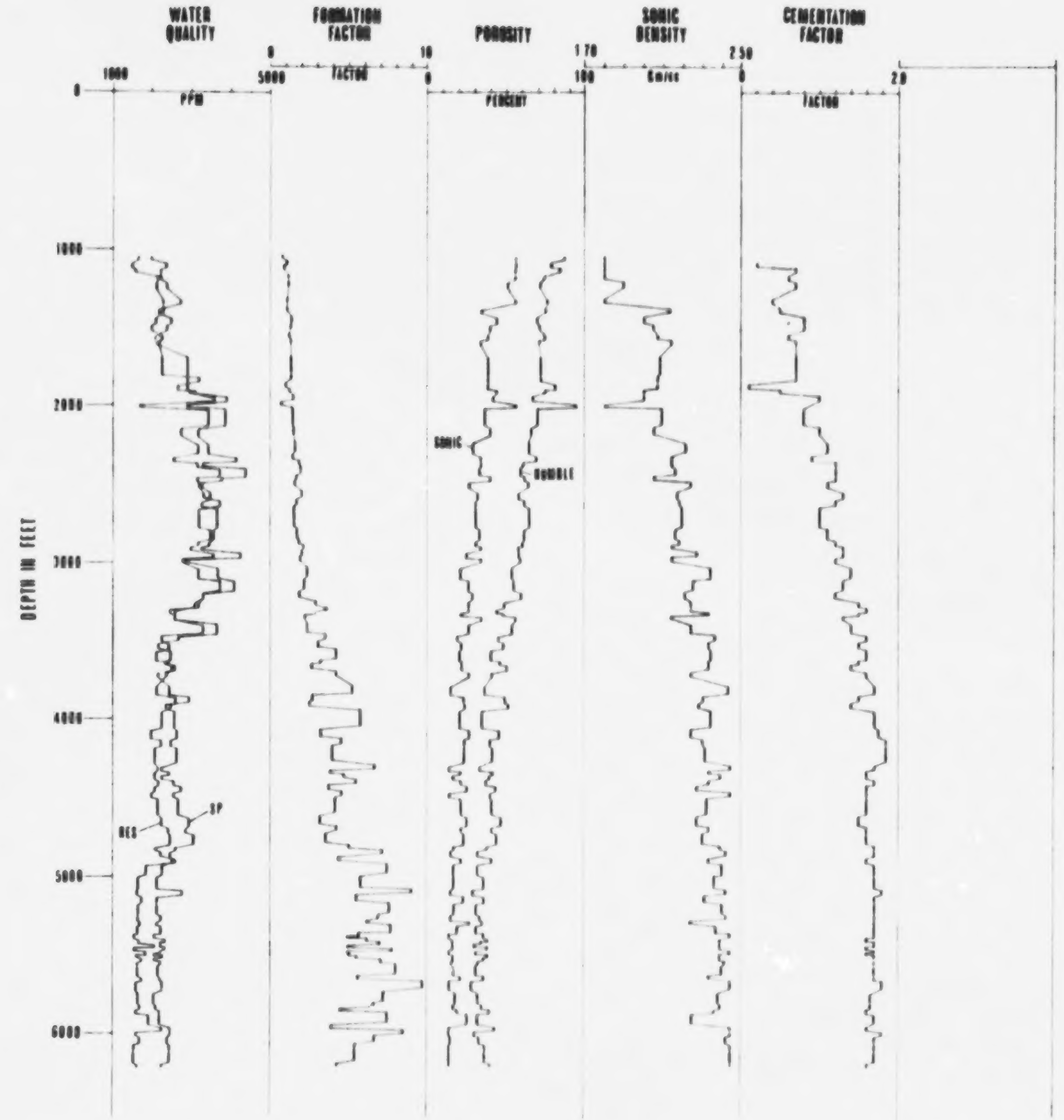
MESA 6-2

Figure 8



COMPUTED CURVES OF LOG
MESA 8-1

Figure 9



LFE CORPORATION Environmental Analysis Laboratories

TLW-6147

FIELD SAMPLING OF RADIOACTIVE GEOTHERMAL EFFLUENTS*

by

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ABSTRACT

A sampling program for radioactive effluents from The Geysers geothermal power plant is described. Radon-222 was sampled both in the non-condensable fraction of geothermal steam and in the atmosphere. A variety of solid and liquid matrices, including steam condensate, cooling tower sludge, soil, and grass, were sampled and analyzed for ^{226}Ra and ^{210}Pb. The three radioactive isotopes ^{222}Rn, ^{226}Ra, and ^{210}Pb are members of the naturally-occurring ^{238}U radioactive decay chain.

Stack sampling techniques were applied to the collection of steam, and a simple sampling train was constructed to separate and collect the condensable and non-condensable fractions. Collection techniques for selected solid and liquid matrices are described. Two complicating factors in the sampling and analysis program are addressed: the collection of atmospheric samples for radon from a local source in the presence of the natural background and the long term temporal variation in the emission rate of contaminants from a geothermal field.

The sampling and analytical methods used are capable of detecting ^{222}Rn, ^{226}Ra, and ^{210}Pb at environmental concentrations that are below the allowable maximums set in State of California regulations.

LFE Environmental Analysis Laboratories
CORPORATION

TLW-6147

FIELD SAMPLING OF RADIOACTIVE GEOTHERMAL EFFLUENTS

I. INTRODUCTION

A monitoring program for radioactive effluents from The Geysers Geothermal Power Plant, Sonoma County, California, was conducted during the summer and fall of 1974. The State of California has set maximum allowable concentrations for the naturally-occurring radionuclides ^{222}Rn in air and ^{226}Ra and ^{210}Pb in water. The purpose of the program was to determine if these allowable concentrations are exceeded. The primary goal was to measure the concentration of ^{222}Rn in power plant emissions. Secondary goals were to measure atmospheric ^{222}Rn concentrations and to measure the concentrations of ^{226}Ra and ^{210}Pb in solid and liquid matrices including steam condensate, drilling mud, cooling tower sludge, surface water, soil, and vegetation. Soil, water, and vegetation samples were collected both at The Geysers and in surrounding communities.

Radon-222, ^{226}Ra, and ^{210}Pb are members of the ^{238}U decay chain which is shown in Table 1.(1) Uranium-238 is present in igneous and sedimentary rocks at average concentrations of 1.2 to 3.9 ppm (parts per million);(2) however, values between 0.03 and 120 ppm have been reported for certain samples.(3) The ^{238}U decay chain involves eight alpha decays and six beta decays (weak branches to other products are not shown) before the stable element ^{206}Pb terminates the chain.

Radon-222, historically called radon, is unique in that it is the only gas in the ^{238}U decay chain. It can diffuse out of soil minerals into the soil gas and then across the soil surface-air interface into the atmosphere. The mean radon exhalation rate is 0.70 atoms/cm^2·sec or 40.0×10^{-18} Ci/cm^2·sec.(4) The concentration of radon in ambient air over the continents ranges from 0.03 to 3.0 pCi/l with an average value of 0.1 pCi/l.(5) Radon in ambient air at The Geysers has three major sources: the surface soil, geothermal steam, and natural fumaroles. Our study emphasized the latter two sources of radon.

Radon itself presents minimal health hazards; but its daughter products are chemically reactive when formed, and they readily attach to other particles in the atmosphere. Some of these particles can be retained in the lung following inhalation. When the attached radioactive isotopes decay, their decay energy is deposited in lung tissue. Of special concern are the short-lived daughters ^{218}Po, ^{214}Pb, ^{214}Bi, and ^{214}Po.(6)

Because of its relatively long half-life of 1600 years, ^{226}Ra in soil can be regarded as an essentially constant source of radon to the air. Lead-210, with a 22 year half-life, blocks the decay chain, at least over the time scale both of our sampling and of developed emissions at The Geysers. The presence of ^{210}Pb in environmental samples at a level above natural background is an indicator of the long term radiological impact of a geothermal power plant.

Site selection techniques are discussed in the next section. Sample collection techniques are presented in Section III. Problems unique to geothermal fields are described in Section IV. The sampling methodology cannot be separated from the analytical methodology; therefore, selected methods are described briefly in an appendix.

II. SITE SELECTION RATIONALE

Selecting the sampling points for ^{222}Rn emission measurements was straight forward. A schematic of a typical power generation system at The Geysers is shown in Figure 1. The well bore is vented directly to the atmosphere both during the drilling stage and during power plant shut down. During normal plant operation, the particle separators, the pressure relief valve, the off gas ejector above the condenser, and the cooling tower are sources of ^{222}Rn emissions. Steam flows through the turbine and into the condenser where it is condensed by direct washing with cooling water. The condensate is then used to wash additional steam. Essentially all of the ^{222}Rn, along with other non-condensable gases, is removed from the condenser by the off gas ejectors, and these gases are released to the atmosphere through a stack approximately 20 to 30 m (60 to 90 ft) high. Therefore, the off gas ejector stacks were expected to be the most significant emission source. A small fraction of the ^{222}Rn dissolves in the scrubbing water and is transported to the cooling towers where the large volume flow of cooling air strips out the radon and then dilutes it upon release to the atmosphere. The radon concentrations both in the air above the cooling towers and within the cooling tower therefore were expected to be low.

Ambient air samples were collected where meteorological conditions and/or topographical features indicated that higher than average radon concentrations might exist. Locations frequently occupied by plant personnel and off-site population centers were also sampled. The on-site and surrounding area sampling locations are shown in Figure 2. Because the winds are predominantly westerly, sampling sites were selected at low points along the Mayacmas Mountains ridge line east of The Geysers. On-site sampling locations included the Union Oil Shop, the Pacific Gas and Electric Company Camp, points downwind of Thermal 4 (a free-venting well), power plant control panels, and the inside of the condensers (which are entered occasionally during plant shutdowns). The closest population centers are the sparsely populated communities in Cobb Valley, Lake County, which is below and east of the Sonoma-Lake County line. Air samples were collected in several of these communities as well as in Cloverdale which is west of The Geysers and served as a control.

Most of the steam condensate is releasedas water vapor from the cooling towers, and approximately 20% is re-injected into wells. A much smaller fraction is discharged to the ground from particle separators and condensate traps. Condensate samples were collected below particle separators, below condensate traps, and in both the cooling towers and off gas ejectors. Water samples were collected in creeks at a time of the year when flows are low but when the relative contributions of fumaroles and steam condensate to the flows are high. Drinking water supplies were sampled both at The Geysers and in surrounding communities.

Soil and vegetation samples were collected in the same general locations as the ambient air samples described previously. Vegetation samples were obtained of the predominant growth types, usually introduced wild grasses, encountered at each location. Soil samples were collected nearby from sparsely vegetated areas in order to facilitate separation of soil from vegetation. Sludge samples were collected in the cooling tower basins.

III. SAMPLE COLLECTION

The sampling train used for collection of steam is shown in Figure 3. The total volume of the tubing is approximately 1 liter. The stainless steel probe was inserted into the flow stream in such a way that only steam passed through the collection train; the high steam flow rates made this simple to achieve. The ice chest was filled with wet ice to condense the steam in the glass coil. The condensate trap forces non-condensable gases up into the collection bag. The system was purged and equilibrated without a collection bag attached for approximately 10 min. or until 10 to 20 cm^3 of condensate had passed through the system. Collection was then initiated and continued until 1 to 2 liter of non-condensable gas had been collected in a Tedlar bag. The condensate, which had been collected in a bottle, was returned to our Richmond facility for ^{210}Pb and ^{226}Ra analyses. The gas was analyzed in a field laboratory for the 3.8 day half-life ^{222}Rn by means of counting in a Lucas cell. The emission concentration of radon was calculated from the known volume of gas counted, the volume of gas collected, and the steam volume sampled (which was calculated from the volume of condensate collected).

Several natural fumaroles were sampled for radon using a modification of the sampling method used for steam. A 20 cm (8 inch) pyrex glass funnel was placed over an area at each fumarole where natural gaseous venting was active. The funnel was "sealed" by placing mud around the bottom edge. From the top of the funnel's stem a polyethylene tube was attached which connected directly to the condensing coil from which the non-condensables were collected in the usual manner. The collection system was equilibrated prior to sampling. Water condensate collected on the walls of the polyethylene tubing and refluxed continually back into the glass funnel, but it was assumed that equilibrium was achieved and that the condensables collected were properly ratioed to the non-condensables.

Ambient air samples were collected at a height of between 1 and 2 m (3 to 6 ft) above ground level. Ambient air was pumped into a Tedlar bag using either a hand pump or a portable mine safety type personal pump. In most cases an integrated sample of 2 liter volume was collected over a period of 10 minutes.

Cooling tower exhaust was sampled using the ambient air technique. Off gas ejector exhaust was sampled using standard stack sampling techniques.(8) Samples were collected through a standard sampling port in the ejector exhaust pipe.

For soil samples a circle of earth of 2 to 4 m (6 to 12 ft) in diameter was selected. The top 2.5 cm (1 inch) of soil at several locations in the shape of a "T" within the circle was removed with a flat-bottomed shovel. The soil was placed in wide-mouth plastic bottles. At the laboratory, the soil was dried at 110° C, the gravel fraction was sieved out, and an aliquot was taken by successively removing alternate sections of the soil pile.

Grasses were cut off at ground level and placed into large plastic bags. In sampling trees and bushes, only the outer leaves were removed.

Water samples were collected in previously cleaned 1 liter polyethylene bottles. No special preservation techniques are required for ^{226}Ra or ^{210}Pb in water. The collection bottle was rinsed a minimum of three times with the water prior to actual sample collection. Surface water samples were taken by immersing the entire bottle. For low flow systems, care was taken not to disturb mud or sediment. Drinking water and steam line condensate were collected by holding a bottle within the flow. Instructions for sampling water are given in both an Environmental Protection Agency Publication(9) and an ASTM Book of Standards.(10) The EPA publication is a handbook for monitoring industrial wastewater, but it is an excellent introduction to water sampling and analysis, especially over an extended time frame.

IV. SAMPLING CONSIDERATIONS

The first problem that we will discuss is the sampling of ambient air for radon. The atmospheric ^{222}Rn concentration away from point sources is a function both of meteorological factors such as wind velocity, the temperature profile, and barometric pressure and of soil conditions such as temperature and moisture content. A 1 to 2% change in barometric pressure produces changes in the ^{222}Rn flux of from 20 to 60%.(11) A drop in soil temperature to below freezing or saturation of the soil with water will decrease the emanation rate.(12,13) The importance of these factors to the design of the sampling program depends upon the relative importance of ^{222}Rn released from geothermal fluid compared to that released from soil within the air basin, the purpose of the monitoring program, and the accuracy of the results desired. If the program purpose is to assess the environmental impact of a geothermal development, then a methodology to distinguish a local source in the presence of a variable background must be designed.

The purpose of LFE Environmental's program at The Geysers was to determine if California state standards for ^{222}Rn in air and for ^{226}Ra and ^{210}Pb in water(14) were being exceeded due to the operation of the generating station. The maximum allowable environmental concentrations for these radionuclides in air and water are shown in Table 2 (there are no concentration limits set for soil by the State of California). These are total concentrations consisting of the natural background component plus the contribution of any local source. These allowable concentrations can be compared with our detection limits which are given in Table 3. For the purposes of this table, the detection limit is defined as that concentration which will yield an integrated number of radioactive decay counts that has a counting error of ± 10%. Numerous definitions of detection limit exist,(15) and therefore one must be careful in making comparisons between the results from different analytical laboratories. Our detection limits are well below the California standards,and therefore the sample sizes and analysis methods used were suitable for the intended purpose. The analysis methods used are capable of counting these radionuclides at concentrations several orders of magnitude above the detection limits.

The variability in the soil emanation rate and the effect of meteorological factors on the radon concentration in an air basin present the possibility of collecting samples at times and places such that samples that are not representative of average concentrations and normal variations are collected. In order to assure state officials that our results would not be below the annual average concentrations, our sampling program was conducted at a time of the year when soil emanation rates would be expected to be high; that is, in the late summer and early fall when the soil is dry and winds are calm. The conditions prevailing at the time of sampling were documented in order to support the validity of the results.

The second consideration is the long term temporal variation in the emission rate of contaminants from a geothermal field. Geothermal effluent rates at Warakei, New Zealand, have been relatively constant over the short term, but they have been variable over the long term exhibiting first increasing and then decreasing behavior.(16) We are not aware of any emission rate data in the literature for The Geysers geothermal field. Therefore, it is difficult to determine the frequency at which an emission source should be sampled for either radon or other potentially hazardous pollutants such as hydrogen sulfide. The recommended frequency of sampling over the short term is a question that is best answered after a preliminary survey has been conducted. A cost-effective field sampling protocol that will produce defensible results can then be formulated.

V. CONCLUSION

Three radionuclides in the ^{238}U decay chain, ^{222}Rn, ^{226}Ra, and ^{210}Pb, are possible environmental contaminants resulting from the utilization of geothermal resources for electricity production. A monitoring program was conducted to assure that the concentrations of these three radionuclides in the environment at and near The Geysers do not exceed the maximum allowable concentrations set by State of California regulations. Methodologies for the sampling of ^{222}Rn in both steam and the atmosphere and for the sampling of ^{226}Ra and ^{210}Pb in solid and liquid matrices were developed. Standard stack, ambient air, water, vegetation, and soil sampling techniques are applicable for the intended purpose at The Geysers Field. It should be kept in mind, however, that steam from this field is relatively free of contaminants. Effluent sampling elsewhere probably will require modifications of the sampling train described.

Atmospheric radon sampling presents special problems because both the geothermal resource and the soil are sources of radon. The background atmospheric radon concentration is a function of a number of topographical, meteorological, and soil variables. The relative importance of these factors depends upon the purpose of the monitoring program. The conditions prevailing at the time of sampling should be documented both as a standard operating procedure and in order to facilitate the interpretation of possible anomalous data.

APPENDIX I

ANALYTICAL METHODOLOGY

A. RADON ANALYSIS

Radon, in either non-condensable gas or ambient air, was determined by means of counting in a Lucas cell.(17) A Lucas cell is a simple instrument consisting of a glass or metal chamber of approximately 100 cm^3 volume that is coated on the inside with ZnS scintillator and a flat glass bottom. Scintillations caused by alpha particles are viewed and counted through the uncoated flat window by means of a photomultiplier tube. The Lucas cell and the associated electronics are of sufficient durability to be used in the field in the back of a pick-up truck.

A potential interference in the radon determination is the presence of ^{220}Rn, historically known as thoron, which is a member of the ^{232}Th decay chain, another naturally-occurring decay chain. Thoron has a short half life of only 55 seconds; therefore if the filling of the Lucas cell is delayed for at least 20 minutes following collection, the thoron has decayed to a negligible quantity. The air is filtered prior to introduction into the Lucas cell in order to remove radon's particulate daughters some of which are also alpha emitters. The cell is filled with a known volume of gas, the scintillations counted, and the data analyzed by a computer program which subtracts background and converts the net counts of radon plus radon daughters to the radon decay rate at the time of collection.

The Lucas cell detection efficiency was determined by de-emanating radon from an aliquot of a National Bureau of Standards ^{226}Ra standard. Carrier gases used were helium and also a mixture of non-condensable gases obtained from a well at The Geysers. Counting efficiencies for alpha emitters are typically 70%.

B. RADIUM-226 ANALYSIS

Radium-226 in water is determined by counting the daughter radon in a Lucas cell. Water is filtered to remove solids, acidified, concentrated, de-emanated, sealed and stored for 10 to 20 days to permit the radon to grow in. The radon is then de-emanated into a Lucas cell for counting.

Soil and vegetation samples are analyzed in the same manner as water samples after dissolution steps.

C. LEAD-210 ANALYSIS

The solution from the de-emanation apparatus is acidified with nitric acid and equilibrated with lead carrier. Lead is precipitated and redissolved in a series of steps in order to remove various impurities. Lead is finally precipitated as lead sulfate, mounted on a counting planchet, and the ^{210}Bi daughter is beta counted periodically over a period of one month. Corrections for counting efficiency and source thickness are made.

ACKNOWLEDGEMENT

The authors are grateful to Mr. William Beeman who directed the field sampling program and modified both sampling equipment and sampling procedures in the field to the specific requirements of our monitoring program.

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*Sampling and analyses funded by the Union Oil Company, Los Angeles, California.

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TABLE 1 URANIUM-238 DECAY CHAIN

Isotope	Half-Life
Uranium-238	4.5×10^9 yr
↓ α	
Thorium-234	24.1 d
↓ β	
Protactinium-234	1.17 min
↓ β	
Uranium-234	2.48×10^5 yr
↓ α	
Thorium-230	8.0×10^4 yr
↓ α	
Radium-226	1.6×10^3 yr
↓ α	
Radon-222	3.825 d
↓ α	
Polonium-218	3.05 min
↓ α	
Lead-214	26.8 min
↓ β	
Bismuth-214	19.7 min
↓ β	
Polonium-214	164 μsec
↓ α	
Lead-210	22 yr
↓ β	
Bismuth-210	5.02 d
↓ β	
Polonium-210	138.3 d
↓ α	
Lead-206	Stable

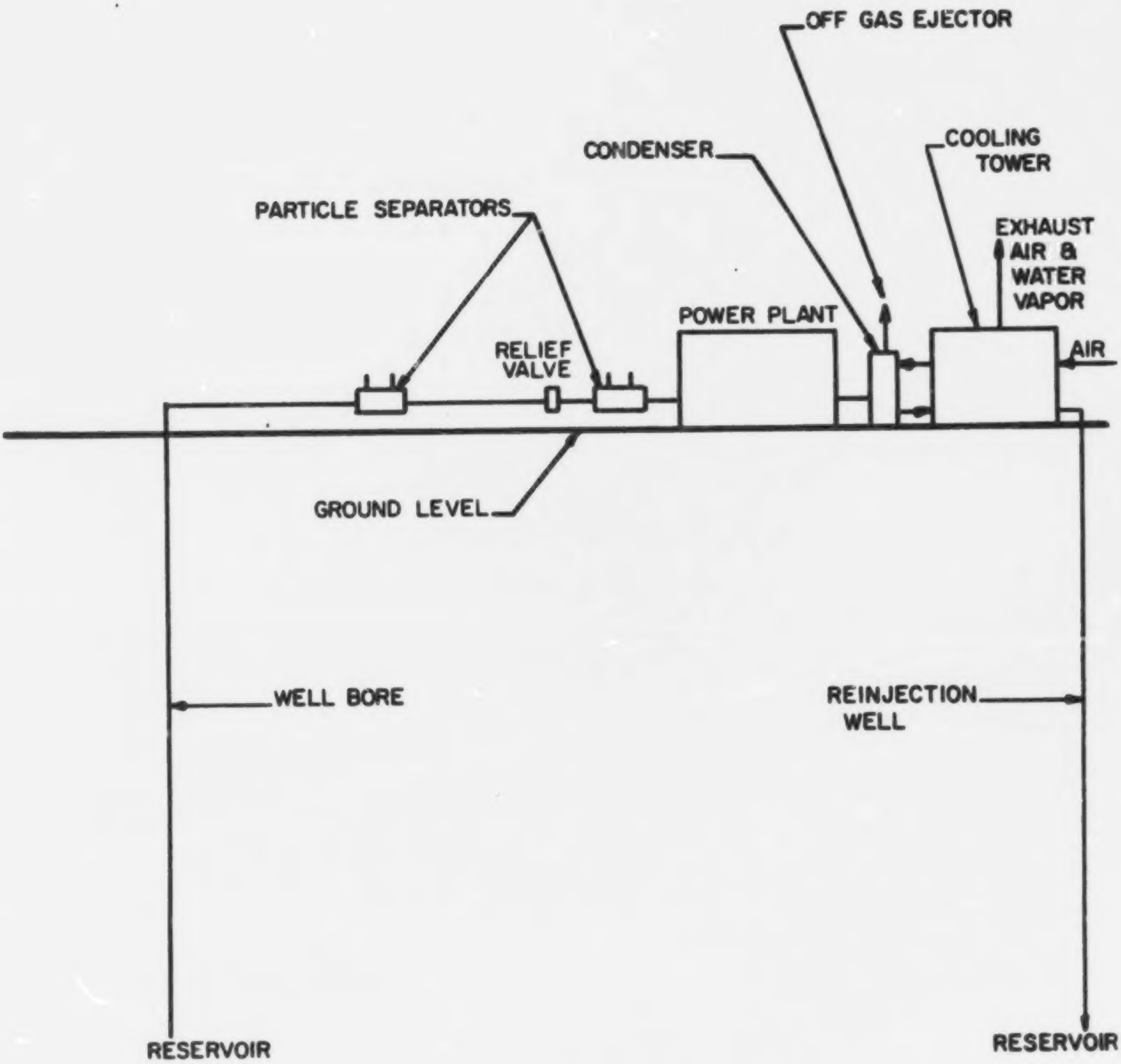
TABLE 2 MAXIMUM ALLOWABLE CONCENTRATIONS FOR ^{222}Rn, ^{226}Ra, AND ^{210}Pb IN AIR AND WATER AS SET BY STATE OF CALIFORNIA STANDARDS

	Concentration Limit (pCi/l)	
	Air	Water
^{222}Rn	3.0	
^{226}Ra	0.003	30
^{210}Pb	0.004	100

TABLE 3 DETECTION LIMITS FOR ^{222}Rn, ^{226}Ra, AND ^{210}Pb IN AIR, WATER AND SOIL

	Detection Limit (pCi/l or pCi/kg)		
	Air	Water	Soil
^{222}Rn	0.1	3.0	
^{226}Ra		0.1	10
^{210}Pb		4.0	200

FIGURE 1 SCHEMATIC DIAGRAM OF THE TYPICAL SYSTEM AT THE GEYSERS.


OFF GAS EJECTOR
CONDENSER
COOLING TOWER
PARTICLE SEPARATORS
EXHAUST AIR & WATER VAPOR
POWER PLANT
RELIEF VALVE
AIR
GROUND LEVEL
WELL BORE
REINJECTION WELL
RESERVOIR
RESERVOIR

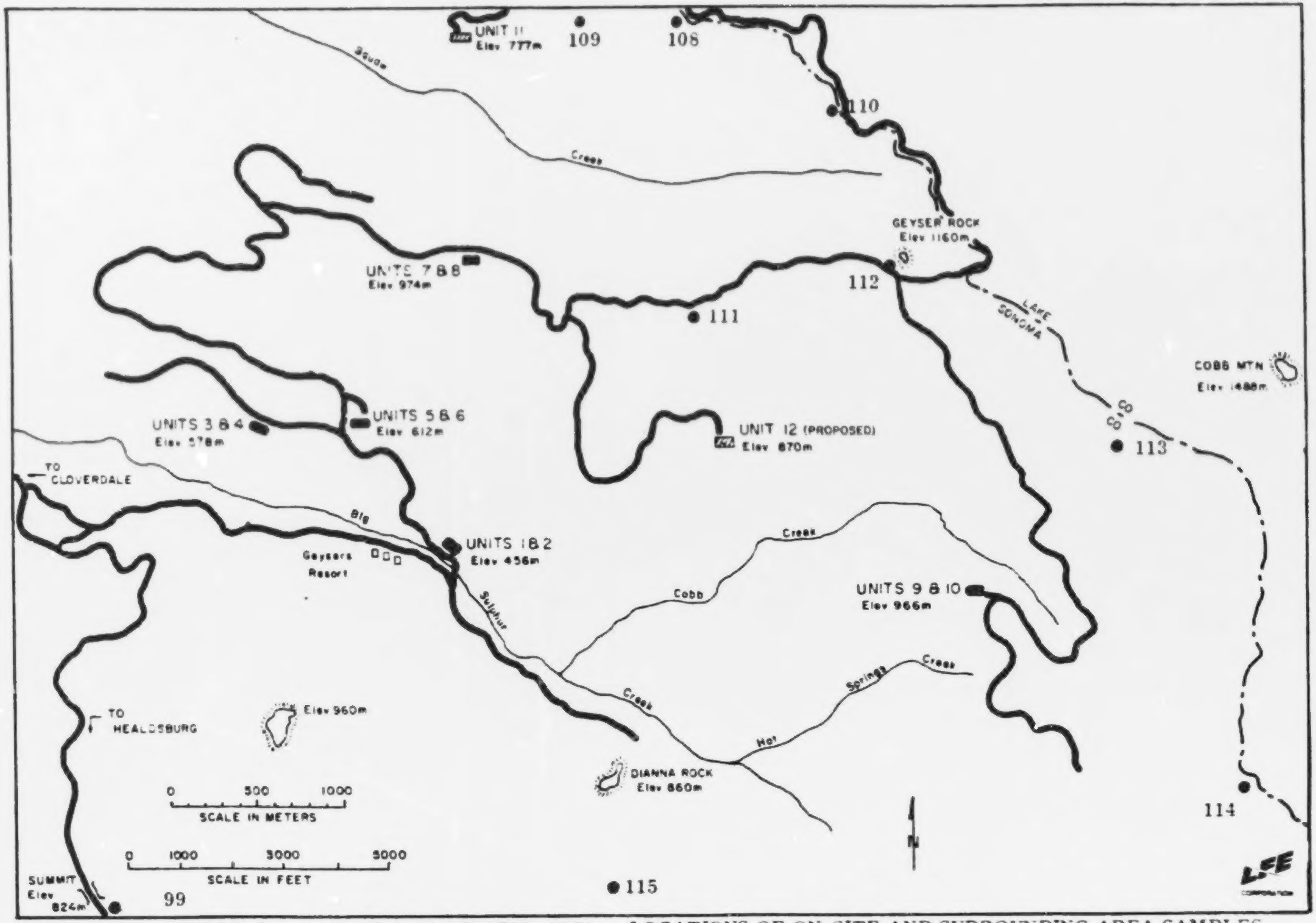

UNIT 11
Elev 777m
109
108
Squaw
Creek
110
GEYSER ROCK
Elev 1160m
112
LAKE
SONOMA
CO
CO
COBB MTN
Elev 1488m
UNITS 7 & 8
Elev 974m
111
UNITS 3 & 4
Elev 578m
UNITS 5 & 6
Elev 612m
UNIT 12 (PROPOSED)
Elev 870m
113
TO CLOVERDALE
Big
UNITS 1 & 2
Elev 456m
Geysers Resort
Sulphur
Creek
Cobb
Creek
UNITS 9 & 10
Elev 966m
Hot
Springs
Creek
TO HEALDSBURG
Elev 960m
DIANNA ROCK
Elev 860m
0
500
1000
SCALE IN METERS
0
1000
3000
5000
SCALE IN FEET
N
114
LFE
CORPORATION
SUMMIT
Elev
824m
99
115

FIGURE 2 MAP OF THE GEYSERS AREA: LOCATIONS OF ON-SITE AND SURROUNDING AREA SAMPLES, for ^{222}Rn

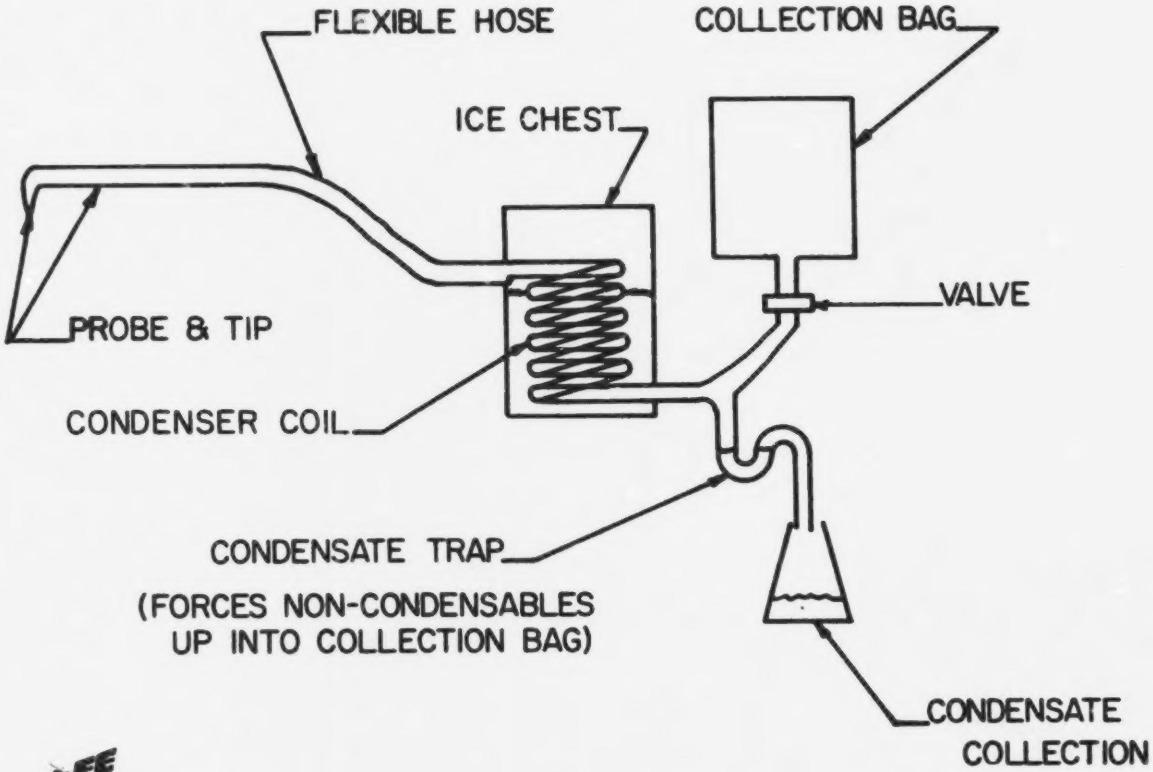

FLEXIBLE HOSE
COLLECTION BAG
ICE CHEST
VALVE
PROBE & TIP
CONDENSER COIL
CONDENSATE TRAP
(FORCES NON-CONDENSABLES
UP INTO COLLECTION BAG)
CONDENSATE
COLLECTION

FIGURE 3 STEAM SAMPLING SYSTEM

SAMPLING HOT SPRINGS FOR RADIOACTIVE AND TRACE ELEMENTS*

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Berkeley, California 94720

INTRODUCTION

The Lawrence Berkeley Laboratory is conducting a program to define parameters for assessment of geothermal resources, and to develop and evaluate techniques to measure these parameters. Field activities, presently underway, combine interrelating geological, geophysical and geochemical studies, leading eventually to choices of sites for deep test holes. As well as furnishing valuable information on the nature of a potential resource, geochemical data provides a baseline upon which the effects of future geothermal developments may be compared.

To date, most of our studies have been centered in northern Nevada where high regional heat flow, numerous hot springs, and available government land combine to furnish satisfactory field test sites. A regional heat flow map, Fig. 1, shows the Battle Mountain High, an area where heat flow exceeds 2.5 μcal cm^{-2} sec^{-1}. Figure 2 illustrates a cutaway model of a geothermal system considered typical of those associated with basin-and-range fault zones. The fault zone furnishes a pathway for meteoric water to percolate deeply into a region of high geothermal gradient, forming a convecting system which occasionally surfaces as a hot spring.

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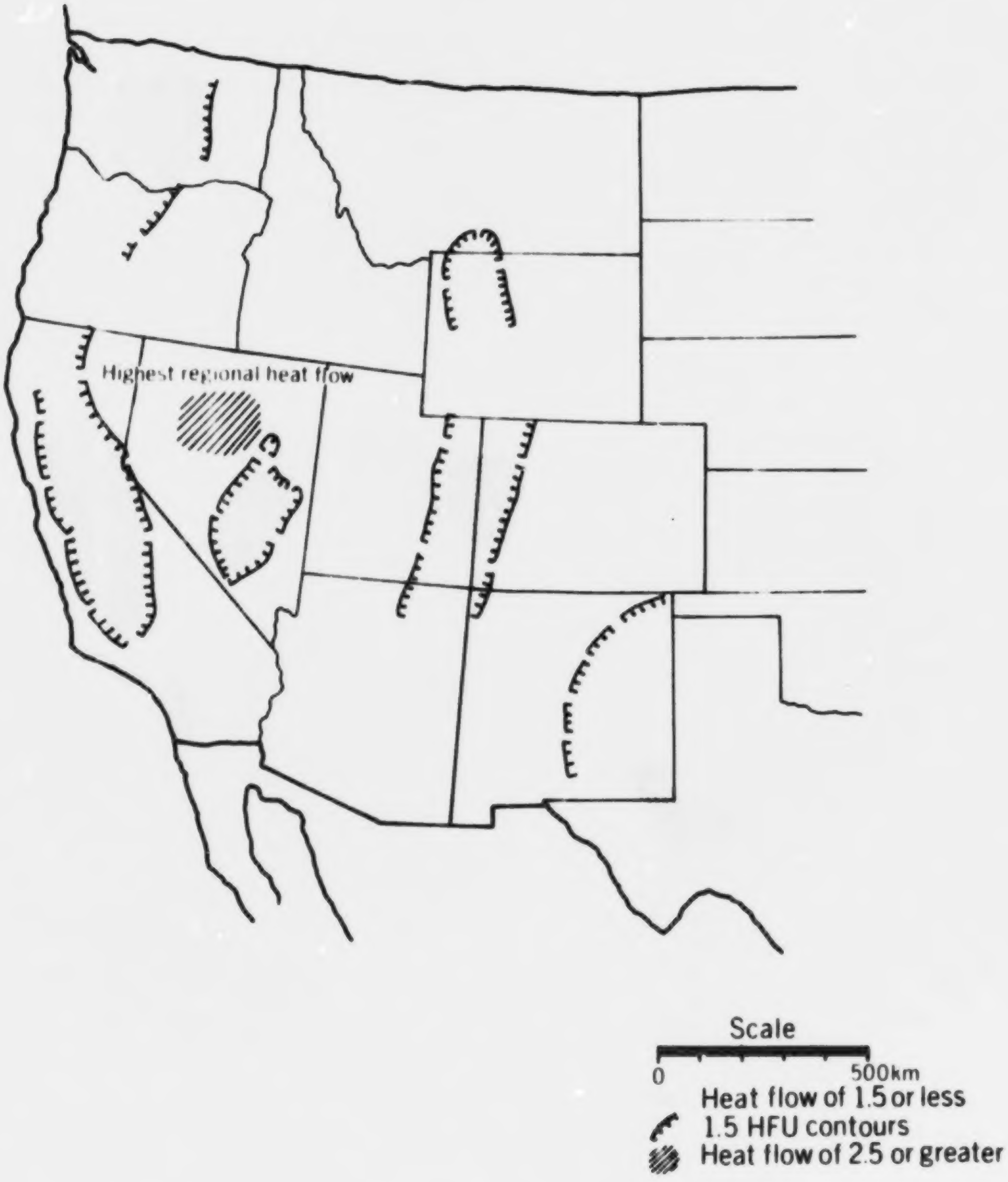
*Work performed under the auspices of the U. S. Energy Research and Development Administration.


Highest regional heat flow
Scale
0
500km
Heat flow of 1.5 or less
1.5 HFU contours
Heat flow of 2.5 or greater

XBL 735 677

Figure 1.

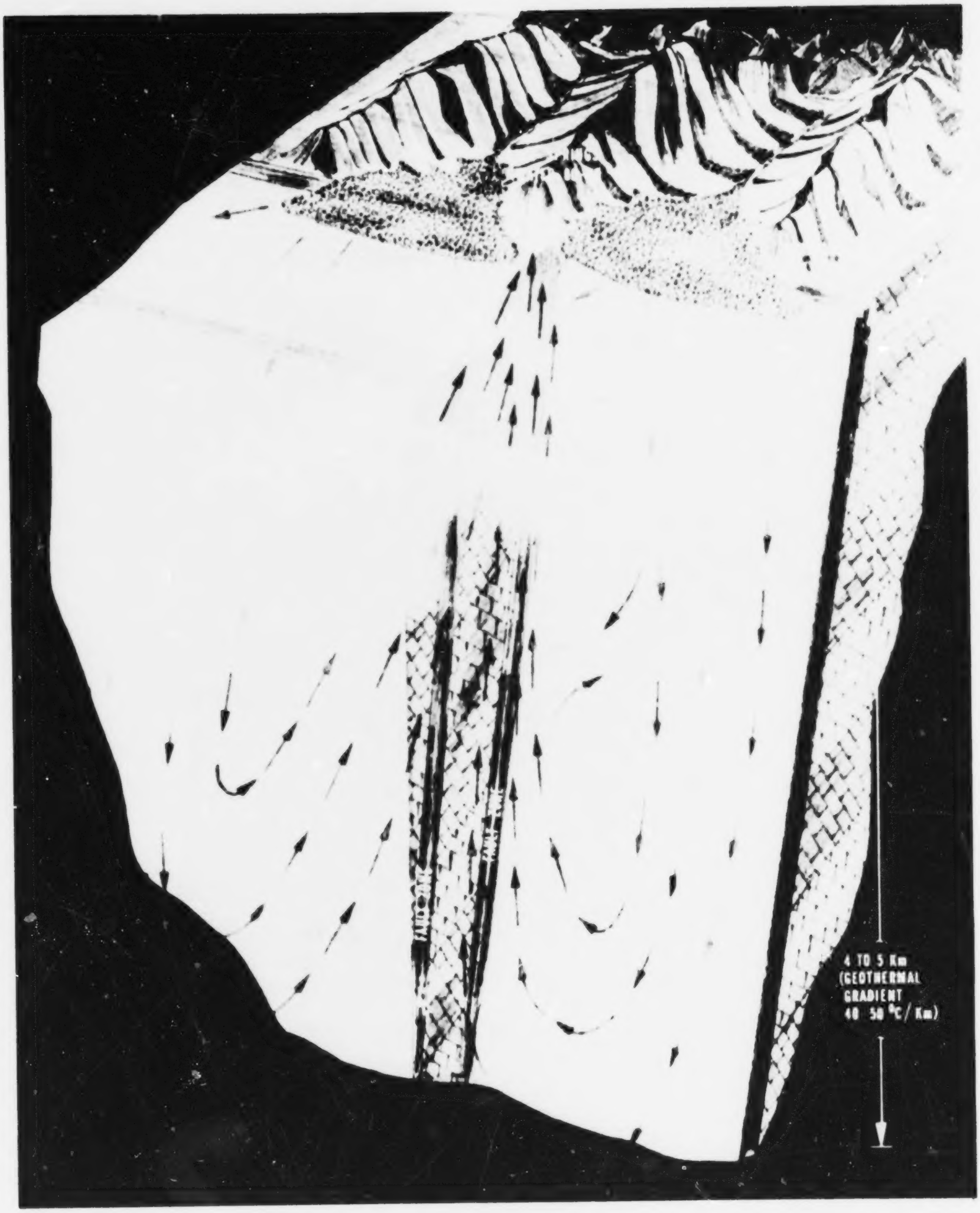

FAULT ZONE
FAULT ZONE
4 TO 5 Km
(GEOTHERMAL
GRADIENT
40 50 °C/ Km)

Figure 2.

SAMPLING FOR MAJOR AND TRACE ELEMENTS

In our geochemical program, water samples are obtained for laboratory radiometry, x-ray fluorescence analysis for major elements (Si, Na, K, Ca, Al, Mg, and S), and neutron activation analyses for trace elements. Collection methods were devised to retain all solid material, including that which precipitates. Major-element data furnishes chemical geothermometry, based on silica- and alkali-element ratios. Besides establishing natural-background baselines, radio- and trace-element contents of hot and cold spring waters, as well as of country rock, may help illuminate the pathways of meteoric water as it flows from its terrestrial origin into hydrothermal systems, and eventually into springs and wells.

Various types of springs sampled are illustrated on Figs. 3, 4, and 5: a hot pool at Big Sulfur Hot Springs, a warm pool at Leach Hot Springs, and a pool below a cold spring east of Kyle, respectively. (Cold springs are sampled because they may represent the groundwater which enters the fault-zone hydrothermal systems.) To a limited extent we have attempted to directly sample blowing wells, as shown on Fig. 6. Chemical geothermometer temperatures from these samples have compared well with reported measured subsurface temperatures.

Frequently, we sample muddy seeps, where only a small flow of water wells up between the cattle hoofprints. At these springs, a 1/4" diameter tygon tube is inserted directly into the flow, and water is drawn with a hand-operated vacuum pump as shown on Fig. 7. Instead of passing into a bottle, the water can also be drawn directly through a 0.45 micron cellulose acetate filter, whose apparatus is shown on Fig. 8. Therefore, water can be introduced to the filter either directly from the spring, or by pumping from a bottle in the field or laboratory. Normally, 500 ml

Figure 3.

Figure 4.

Figure 5.

Figure 6.

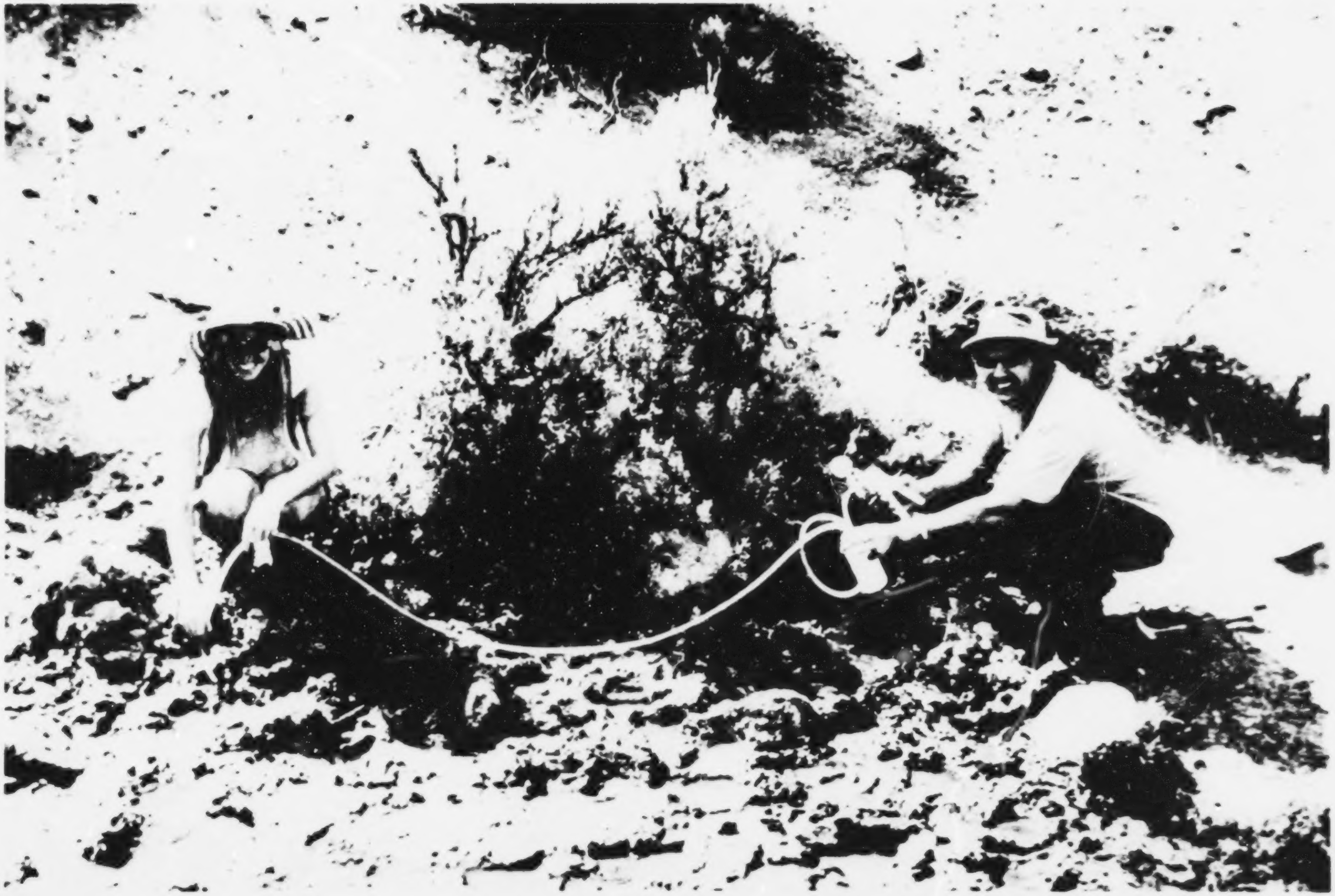


Figure 7.

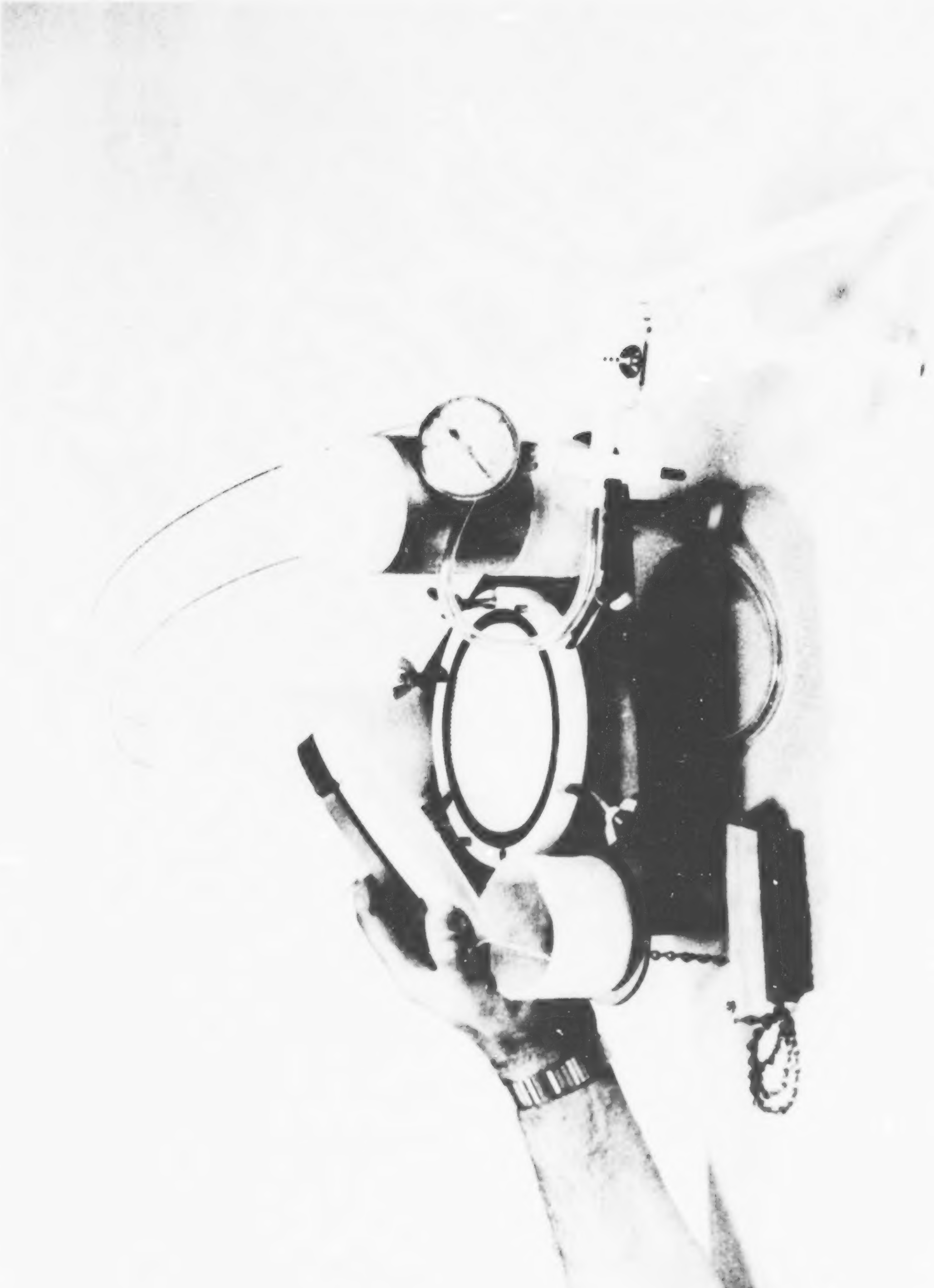


Figure 8.

Nalgene bottles are used to collect and store the samples. These field sampling techniques, and laboratory analytical methods and results, are described in detail in papers by Bowman et al. (1974, 1975), and Hebert and Bowman (1975).

In the field or laboratory, drops of filtered water are evaporated onto a lexan disc, with a fixing solution, for subsequent x-ray fluorescence analysis. (After the x-ray fluorescence analysis, the lexan can be irradiated, cleaned and etched for determination of the water's uranium content.) Evaporation in the field is shown on Fig. 9, and the resulting disc on Fig. 10.

For H_2S determinations, a silver disc is placed in an unfiltered aliquot of each water sample. The disc is later analyzed for sulfur by x-ray fluorescence. Figure 11 shows the response of x-ray intensity to H_2S by this method.

Filtered samples for neutron activation analysis are obtained by evaporating the water directly from the Nalgene bottles (at 80°C) in the laboratory. The resulting residue is incorporated with a plastic binder into a pellet, and irradiated along with standards in a research reactor at the University of California, Berkeley.

Some results of the neutron activation method are illustrated on Figs. 12 and 13; Fig. 12 illustrates the contrast in uranium contents of hot and cold spring waters, and Fig. 13 the levels of some trace elements in pools of differing temperature at Buffalo Valley Hot Springs.

RADIOACTIVE EFFLUENTS

Prior to sampling, a gamma survey of the spring area is conducted using a portable NaI(Tℓ) detector, shown on Fig. 14. Samples for

Figure 9.

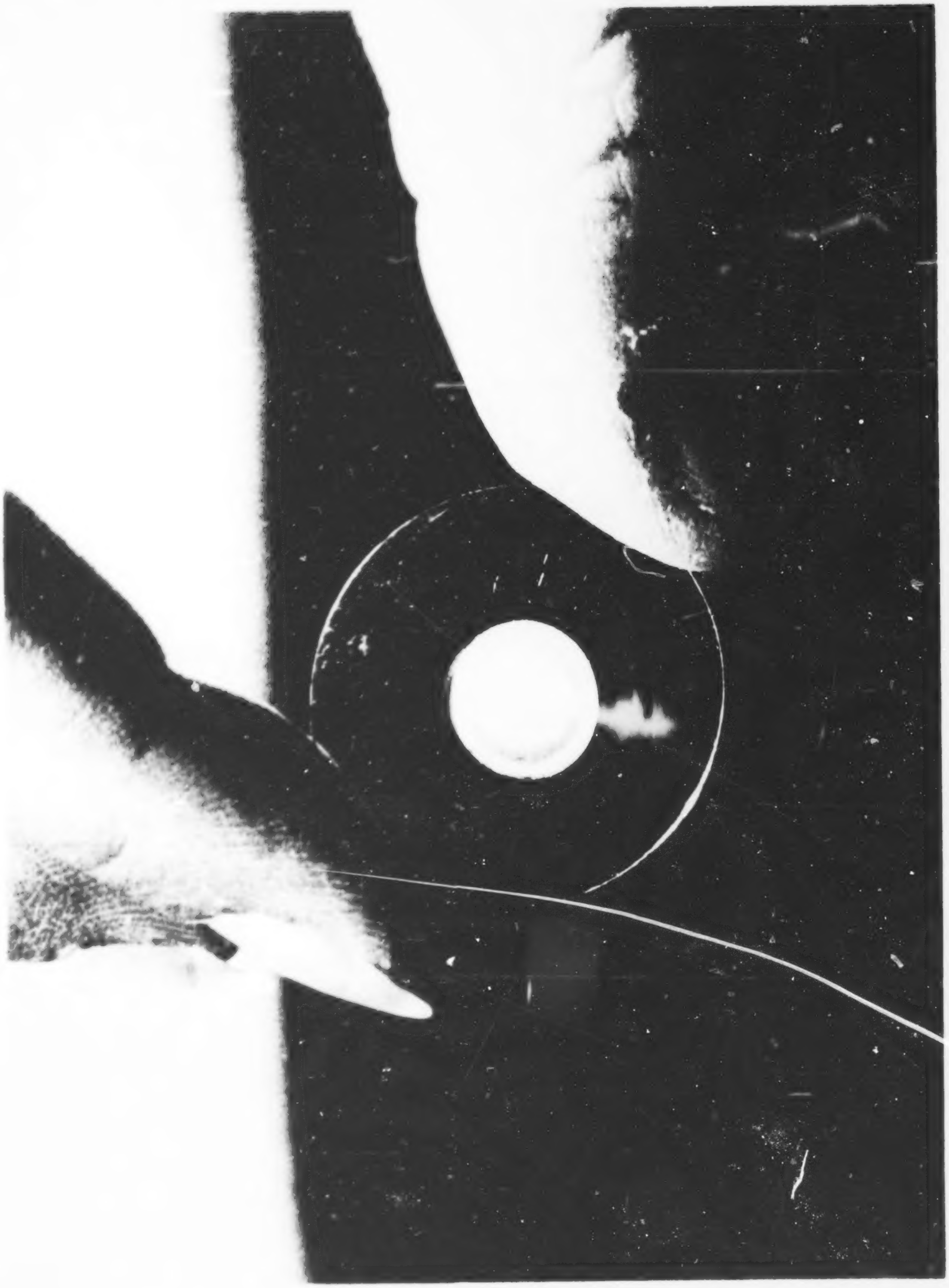


Figure 10.

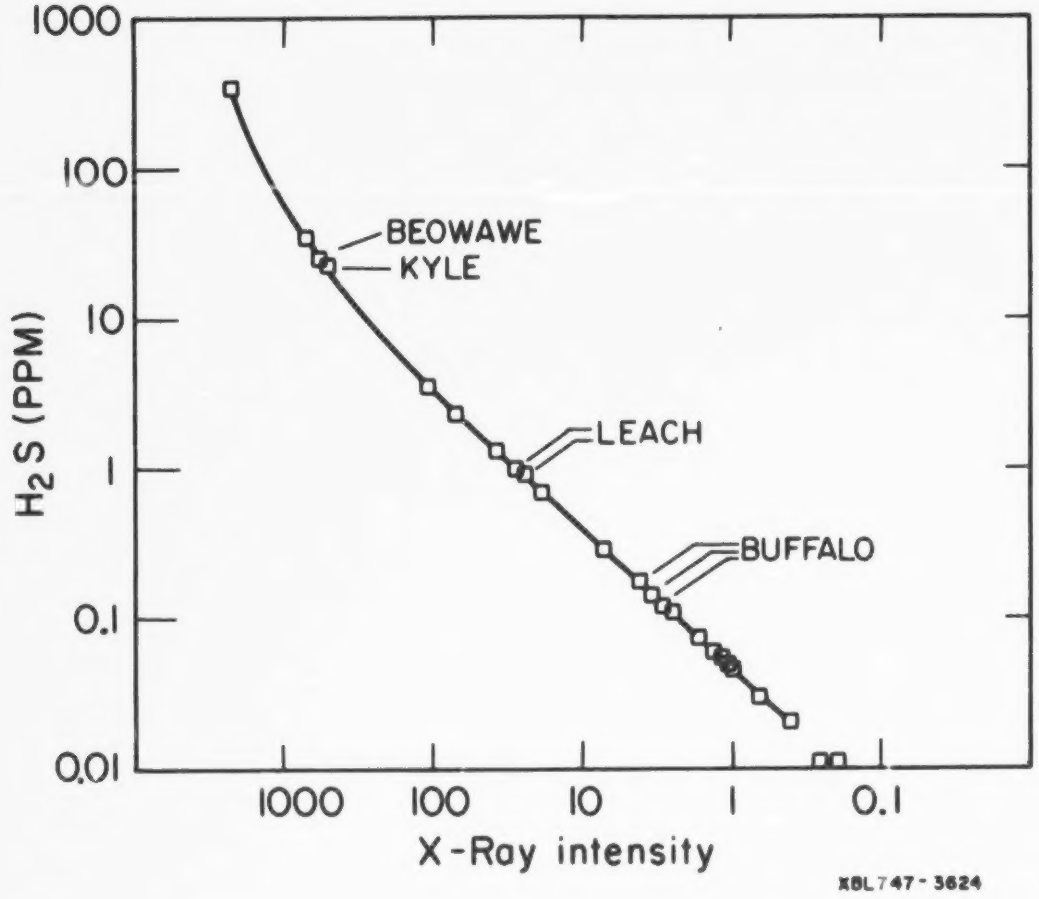

1000
100
10
1
0.1
0.01
H_2S (PPM)
1000
100
10
1
0.1
X-Ray intensity
BEOWAWE
KYLE
LEACH
BUFFALO
XBL747-3624

Figure 11.

URANIUM (PPB)
Hot and Cold Springs

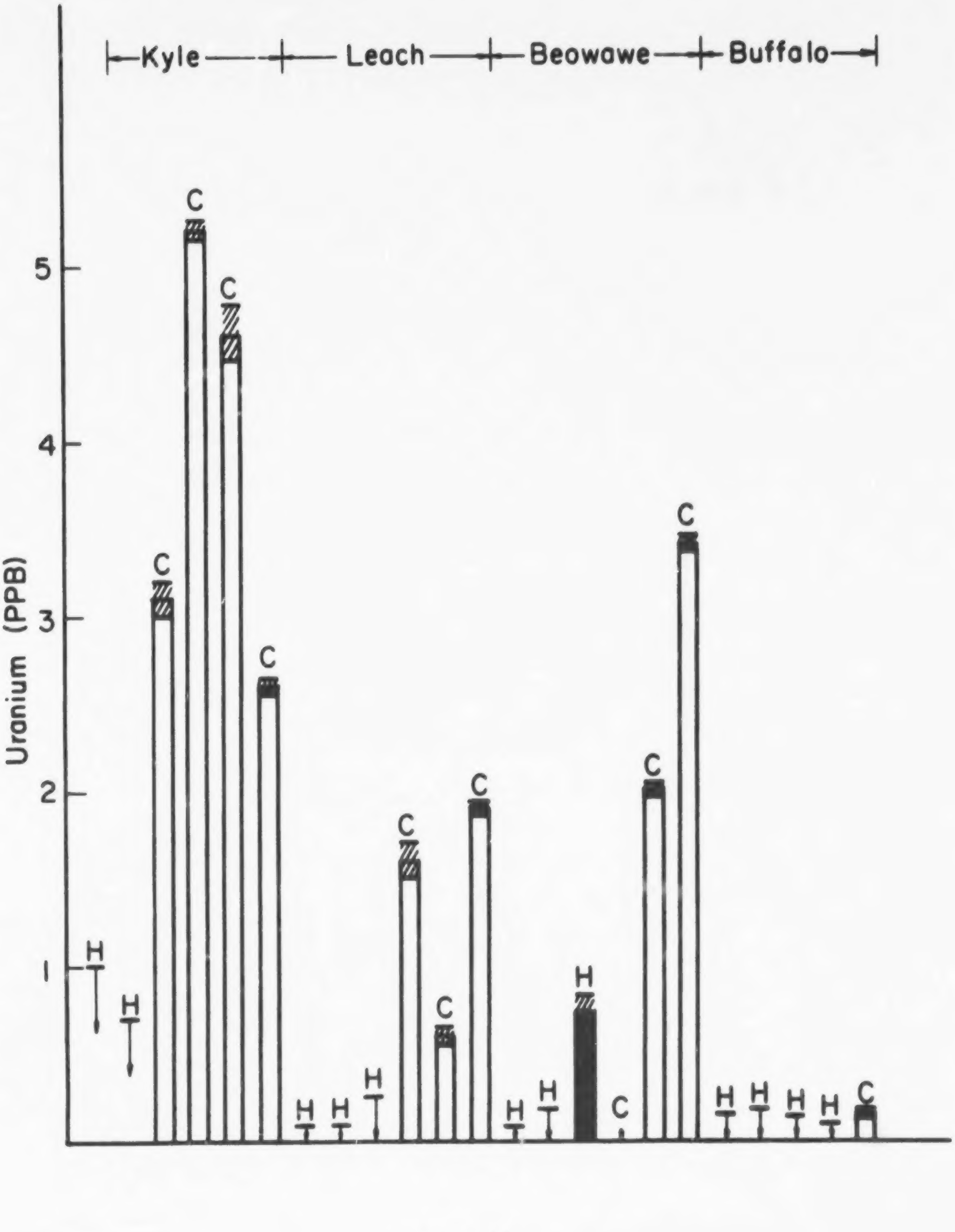


Figure 12.

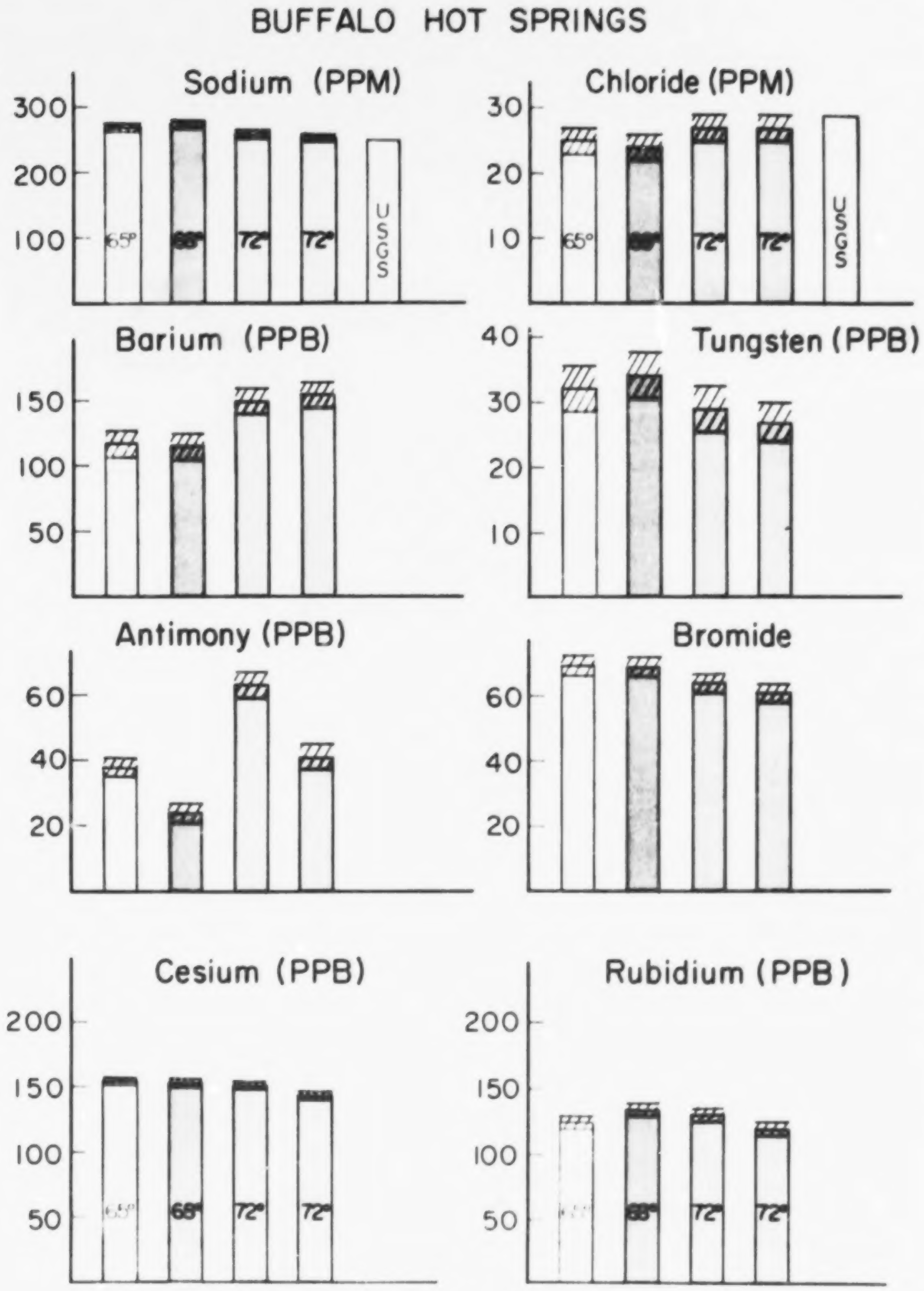

BUFFALO HOT SPRINGS
Sodium (PPM)
300
200
100
65°
68°
72°
72°
USGS
Chloride (PPM)
30
20
10
65°
68°
72°
72°
USGS
Barium (PPB)
150
100
50
Tungsten (PPB)
40
30
20
10
Antimony (PPB)
60
40
20
Bromide
60
40
20
Cesium (PPB)
200
150
100
50
65°
68°
72°
72°
Rubidium (PPB)
200
150
100
50
65°
68°
72°
72°

Figure 13.

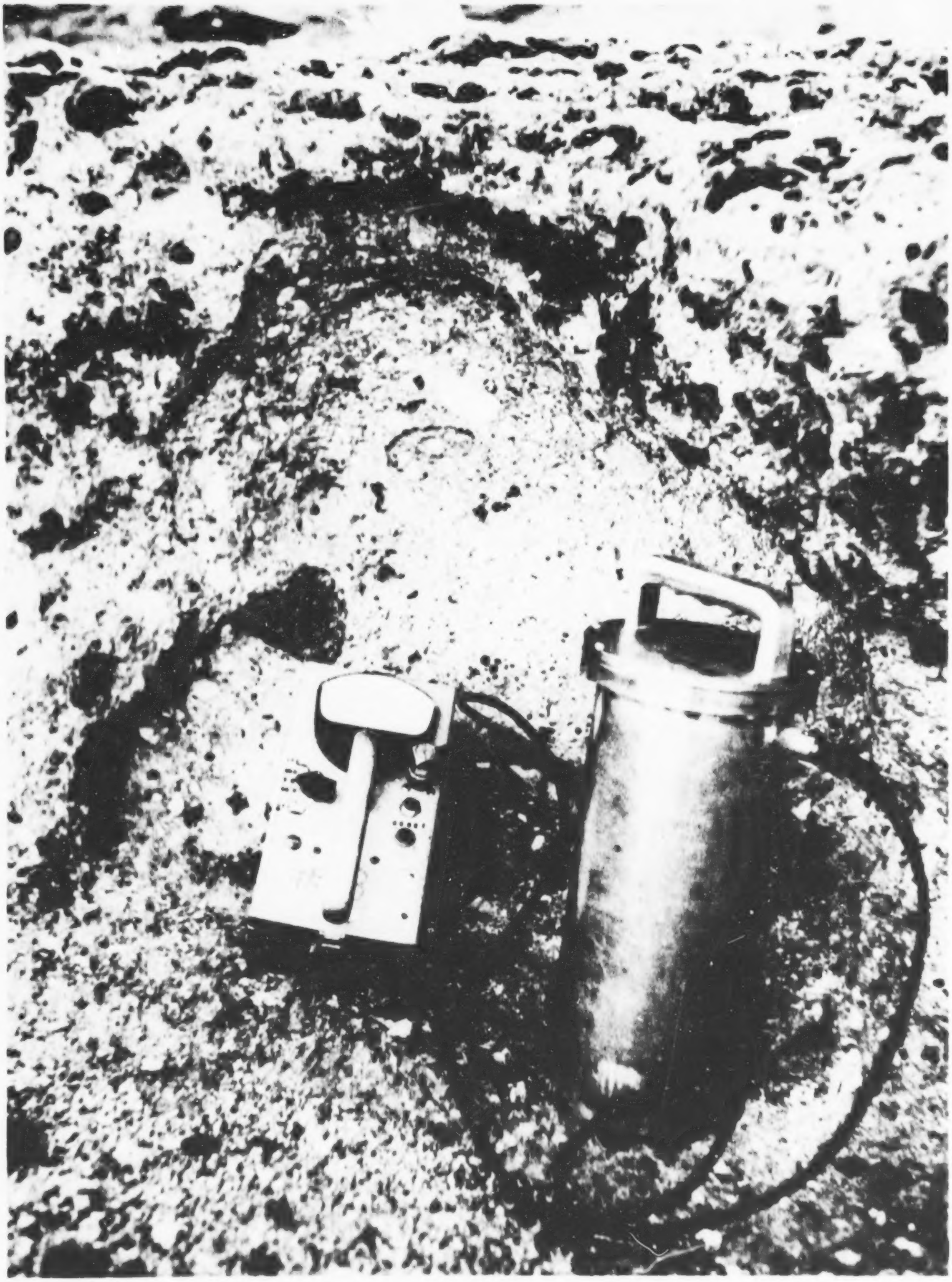


Figure 14.

laboratory radiometry are usually collected by scooping the spring water directly from the pools into Nalgene bottles. This minimizes radon loss which might occur if the water were drawn through the filter system. Bottle lids are immediately taped, and samples transported to the laboratory for gamma-ray pulse-height analyses. The time of sampling is carefully noted, to account for the radioactive decay of ^{222}Rn (3.8-day half-life) between sampling and gamma counting. With a reasonably short interval between sampling and counting, sensitivity of this method is of the order of a few tens of pCi per liter of ^{222}Rn. Along with spring waters, spring wall sinter, tufa, and muck are collected, for subsequent laboratory gamma-ray analyses. This provides comparison of the contents of radium and other radioelements with the ^{222}Rn content of the water.

A sampling system for radon emanating in and around a spring system utilizes alpha-track detectors. This method integrates radon emanation over a long time period, minimizing short-term fluctuations in response to changes in atmospheric conditions. The detectors are inverted plastic cups with specially treated dielectric alpha-sensitive plastic wafers attached inside, as shown on Fig. 15. They are placed, each in an approximately 0.5 meter deep hole, then covered. After several weeks' exposure, the cups are retrieved, detectors removed, etched, tracks counted, and normalized track densities calculated. This service, used primarily by the uranium industry, is provided by Terradex Company in Walnut Creek, California. Resulting track densities in the vicinity of Buffalo Valley Hot Springs, are shown on Fig. 16, and point out the sharp variations in radon emanation at that site. Figure 17 illustrates the contours of radon emanation over a broader area of Buffalo Valley. More detailed descriptions

TRACK ETCH RADON DETECTOR

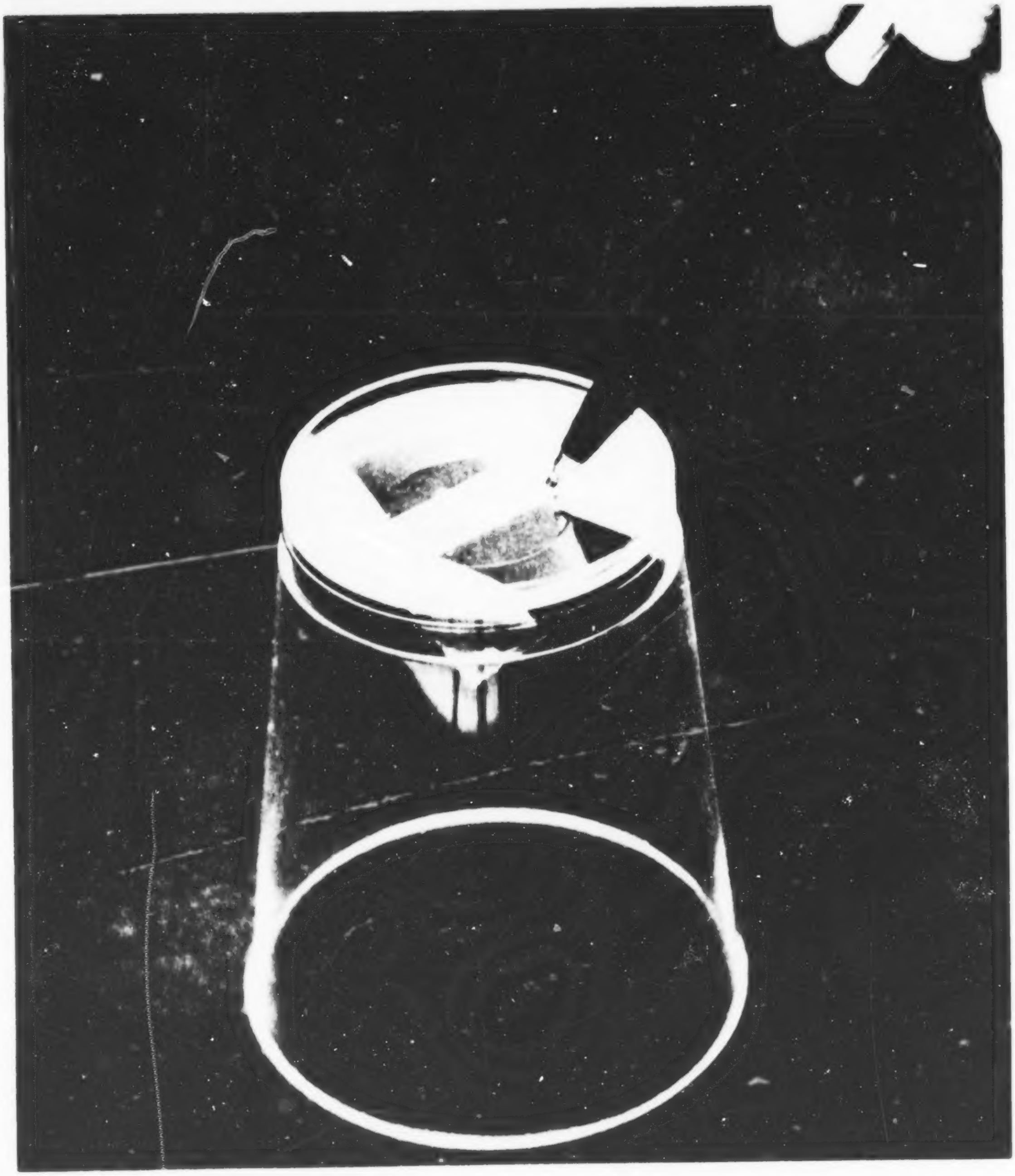


Figure 15.

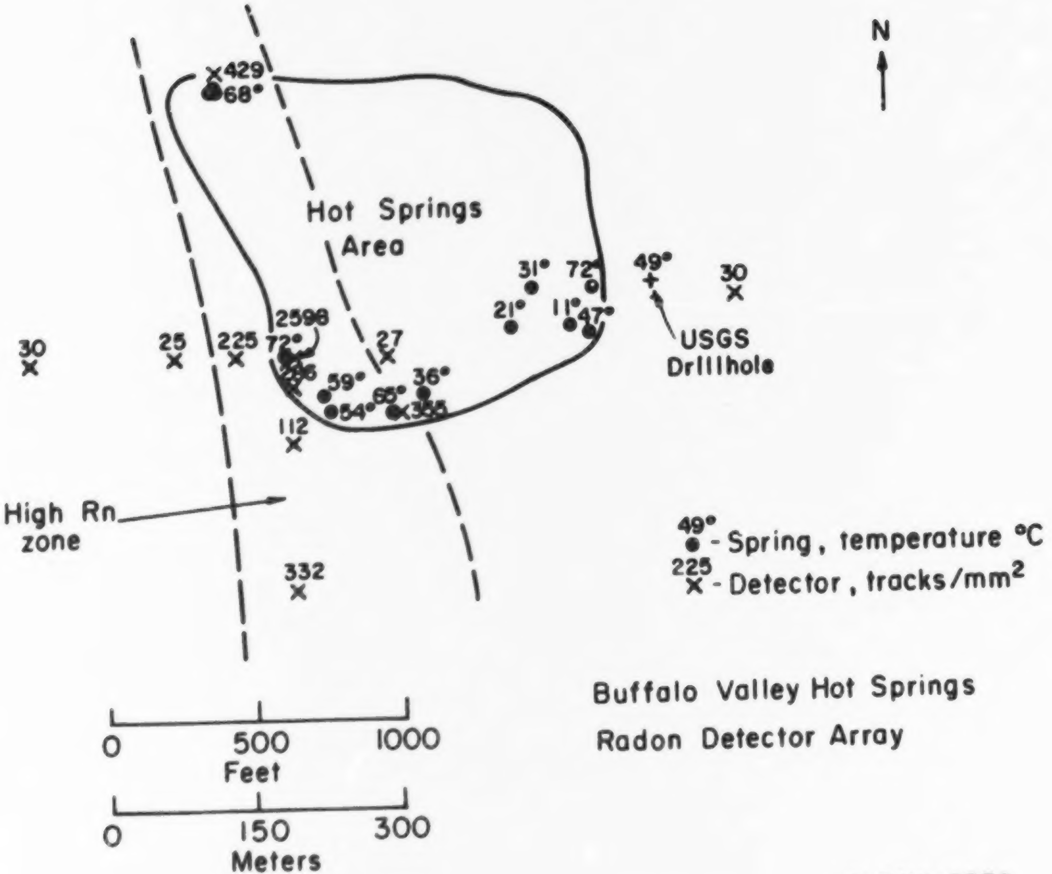
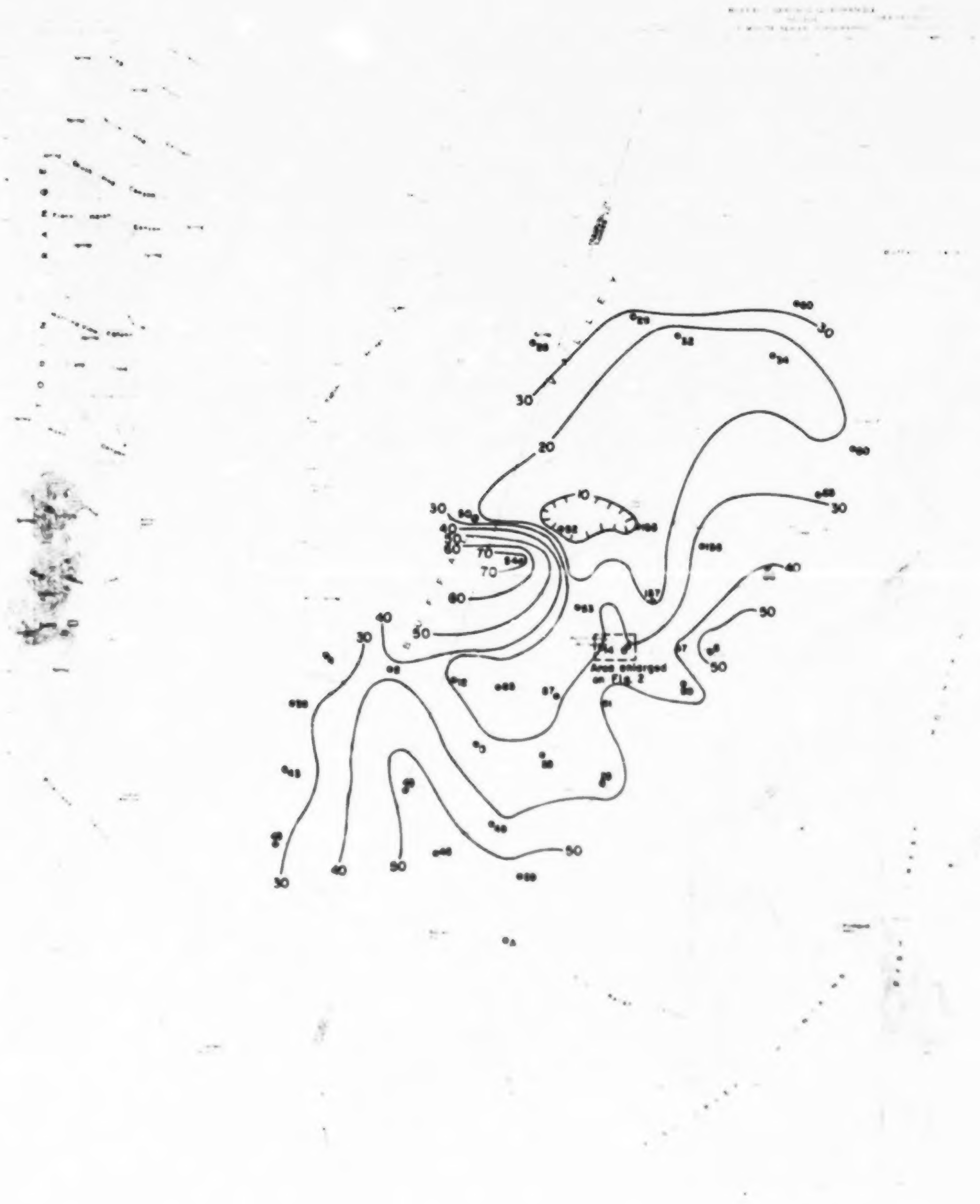

N
X429
68°
Hot Springs Area
31°
72°
49°
30
21°
11°
47°
USGS Drillhole
2598
72°
30
25
225
27
59°
36°
65°
54°
356
112
High Rn zone
332
49° - Spring, temperature °C
225 X - Detector, tracks/mm²
Buffalo Valley Hot Springs
Radon Detector Array
0
500
1000
Feet
0
150
300
Meters
XBL 7412-8379

Figure 16.


30
30
20
10
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40
50
60
70
70
80
40
50
30
40
50
30
40
50
50
Area enlarged on Fig. 2

Figure 17.

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of radiometric methods and results are provided in papers by Wollenberg (1974a and b, 1975).

SUMMARY

The techniques described briefly here have proved successful in obtaining samples of hot and cold spring waters for x-ray fluorescence, neutron activation, and radiometric analyses. These sampling methods require only lightweight, portable field apparatus, and do not involve lengthy collection procedures. Good flexibility in field operations is necessary to accommodate the widely varying conditions of temperature, flow, and accessibility encountered at the different spring sites.

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UNION OIL COMPANY OF CALIFORNIA'S GEOTHERMAL SAMPLING TECHNIQUES

by

D.J. Christoffersen, R.N. Wheatley, and J.A. Baur

Introduction

The purpose of this paper is to describe the procedures used by Union Oil Company to sample and analyze produced geothermal steam for total composition.

As is the case in any analytical problem, representative, accurate sampling is essential to the problem solution. Sampling produced geothermal steam is no exception to this rule. We are dealing with a sample matrix which is mainly water and analyzing for gaseous and other compounds some of which are highly soluble in water and some of which are relatively insoluble. The usual components of geothermal steam, in addition to water, are shown in Figure 1 and the sampling and analysis for these compounds is described below.

Sampling Apparatus

Our sampling train is shown schematically in Figure 2 and photographically in Figure 3. This system is used for two purposes. First of all it is used to obtain an accurate measure of the "non-condensible" gas content -- necessary for total composition calculations. Non-condensible gases being defined in this case as those compounds which remain in the vapor phase after passing through a 0°C condenser and water contact. Included are small amounts of relatively water insoluble compounds such as hydrogen, nitrogen and methane and also a portion of water soluble gases such as carbon dioxide, hydrogen sulfide and ammonia. Secondly, the train is used to obtain representative samples for analysis.

For determining the non-condensible gas content of steam, the sample system is set up on location and the insulated container holding the condenser coil is filled with ice water and the condenser disconnected from the sample train. The condenser coil is connected to the steam line via a by-pass valve by means of a 25-foot flexible, stainless steel tubing using appropriate fittings at both ends. The by-pass valve is positioned to vent with no flow to the condenser and the sample port valve on the steam line is fully opened. After flowing steam through the connecting tubing for sufficient time (usually 10 to 15 minutes) for the tubing to come to temperature, steam is valved to the disconnected condenser until a condensate flow rate of about 50 ml/min is obtained. Approximately one liter of condensate is purged through the condenser. This allows the condenser system to come to an equilibrated condition and also cleans the tubing of any possible residue or contamination from prior samplings.

Wet test meters must be properly equilibrated to prevent absorption of gases such as carbon dioxide for accurate volume measurements. This is done by attaching the equilibrated condenser to the sample train and passing the non-condensible gases through the wet test meter for 10 to 15 minutes. The condenser is disconnected from the sample train. The collection bottle is replaced by a tared one-quart bottle and the wet test meter reading is noted. The condenser is quickly attached to the sample train by means of rubber tubing and actual sampling begins. Sampling continues until the collection bottle is filled or 3 to 4 liters of non-condensible gas volume is reached. The condenser is then disconnected from the train and the non-condensible gas content of the steam determined from the weight of water collected and the volume of gas measured after appropriate corrections for temperature and barometric pressure.

The condenser system is then maintained in equilibrium and used for collection of analytical samples. Sampling bottles containing appropriate chemical fixing reagents for collection of reactive compounds are inserted in place of the condensate collection bottle. A gas sampling cylinder is placed between the bottles and the wet test meter for sampling non-reactive gases. Analysis samples are described in detail below.

There have been cases where equipment such as described here has not been available for field use. In these instances we have used an improvised method substituting measurement of the volume of non-condensible gases by water displacement in a graduated cylinder and collection of non-condensible gases using the device shown in Figure 4.

Collection of Analytical Samples and Their Analysis

Gas samples are collected in 250-ml glass cylinders by the procedure described above. The composition of the gas is determined by a Union Oil mass spectrometry method accurate to ±2% relative or ±0.1% absolute, whichever is greater.

For the determination of ammonia a quart bottle containing a weighed volume (approximately 200 ml) of 0.1N hydrochloric acid and 4 drops of methyl orange is inserted in the sample train in place of the condensate bottle. Condensate and gas pass through a glass frit immersed in the solution quantitatively removing ammonia from both phases. Sampling continues until approximately 200 ml of condensate has been collected and the bottle is then removed from the train for weighing and analysis. The analysis procedure consists of making the solution alkaline, distillation into boric acid followed by titration with standard hydrochloric acid.

For the determination of hydrogen sulfide, a 1-quart bottle containing a weighed volume (approximately 100 ml) of 15% neutral cadmium sulfate is placed in the sample train. Condensate and gas contact this solution after passing through an immersed glass frit and hydrogen sulfide is quantitatively removed from both phases. Sampling continues until approximately 100 ml of condensate have been collected. (A second "check flask" of cadmium sulfate in series can be used to make certain there is no H_2S carryover.) The bottles are then removed from the train, weighed, and analyzed. The analysis procedure consists of adding excess standard iodine, acidifying and back titrating with standard thiosulfate. Take care to include any cadmium sulfide adhering to the glass frit in the analysis.

Samples for carbon dioxide analysis are obtained by placing two one-quart bottles containing weighed volumes (approximately 200 ml each) of 1N sodium hydroxide in series in the sample train to quantitatively remove carbon dioxide from condensate and gas. The inlet to each bottle is a glass frit immersed in the solution. After collection of approximately 100 ml of condensate, remove the bottles from the sample train, weigh and analyze. The analysis procedure determines carbon dioxide by acidification with sulfuric acid, evolution, absorption on ascarite, and weighing the ascarite.

A summary of the analytical methods used is given in Figure 5.

Calculations

The calculations required are relatively straightforward and proceed as follows: The weight percent of collected non-condensible gases is derived from the measured volume of gas, average molecular weight of the gas as determined by mass spectrometry and appropriate temperature, pressure corrections (i.e., the actual weight of the non-condensible volume) compared to the same number plus the condensate weight. Similarly the volume percent of the non-condensibles is calculated by comparing the corrected volume of non-condensibles to this same volume plus the calculated gaseous volume of the condensate.

The weight % of inert (as opposed to collected) non-condensibles methane, hydrogen, nitrogen and argon is calculated from their mass spectrometrically determined concentrations in the gas phase, measured gas volume, and known molecular weights compared to the determined total sample weight. Similarly the total sample basis concentrations of chemically analyzed absorbed ammonia, hydrogen sulfide and carbon dioxide are calculated from determined concentrations, known sample weights and relationship of condensate to total sample weight from above.

Additional Comments

The sampling scheme described is one which is used on a "dry" brine-free steam. In those cases where the produced steam has a high dissolved solids content, exactly the same procedure is used except that a separator is used to remove brine ahead of the sampling train. Figure 6 is a photograph of such a separator in action in the field.

Figures 7 and 8 are photographs of our sampling vehicle and a field laboratory at The Geysers field in California's Sonoma County.

FIGURE 1 - Components Sought in Steam Compositional Analysis

COMPONENTS SOUGHT iN STEAM COMPOSITIONAL ANALYSIS

AMMONIA
CARBON DIOXIDE
HYDROGEN
HYDROGEN SULFIDE
"INERT" GASES
METHANE
NITROGEN

FIGURE 2 - Steam Sampling Apparatus

STEAM SAMPLING APPARATUS

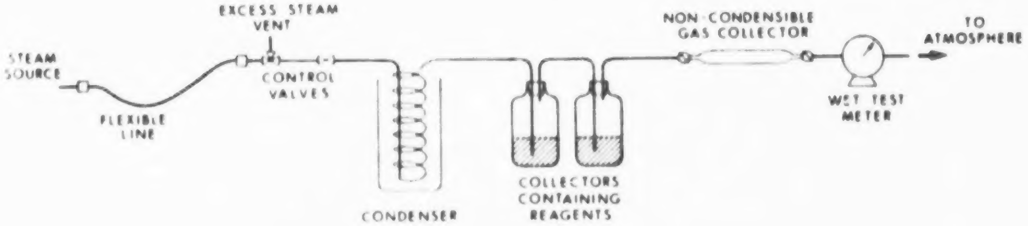
STEAM SOURCE
FLEXIBLE LINE
EXCESS STEAM VENT
CONTROL VALVES
CONDENSER
COLLECTORS CONTAINING REAGENTS
NON-CONDENSIBLE GAS COLLECTOR
WET TEST METER
TO ATMOSPHERE

FIGURE 3 - Steam Sampling Apparatus

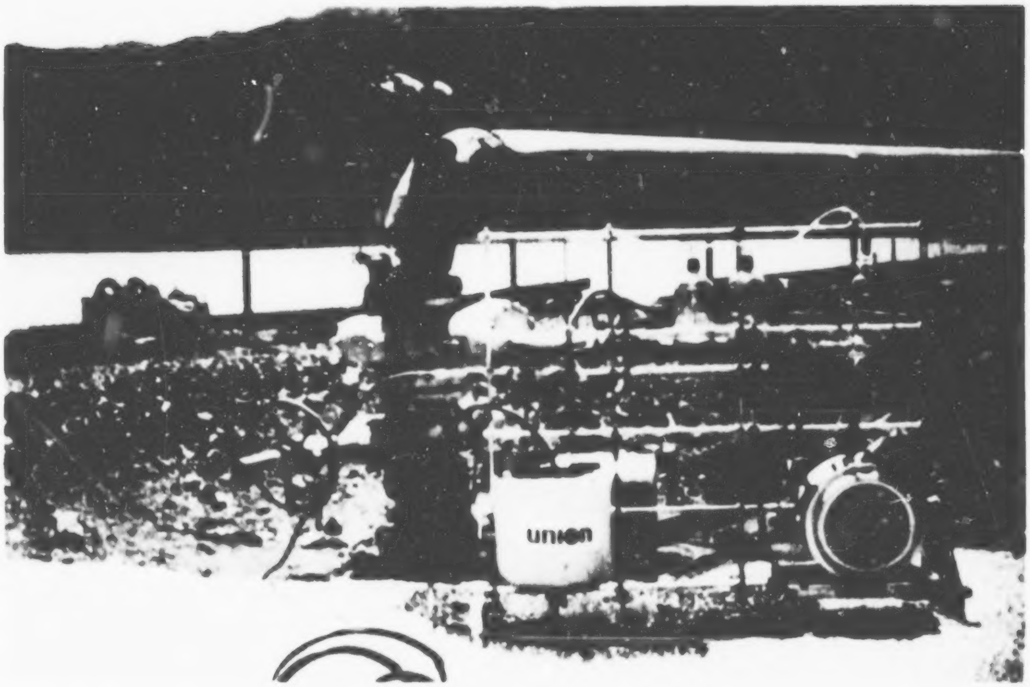

FIGURE 4 - Collection of Air Free Gas Samples

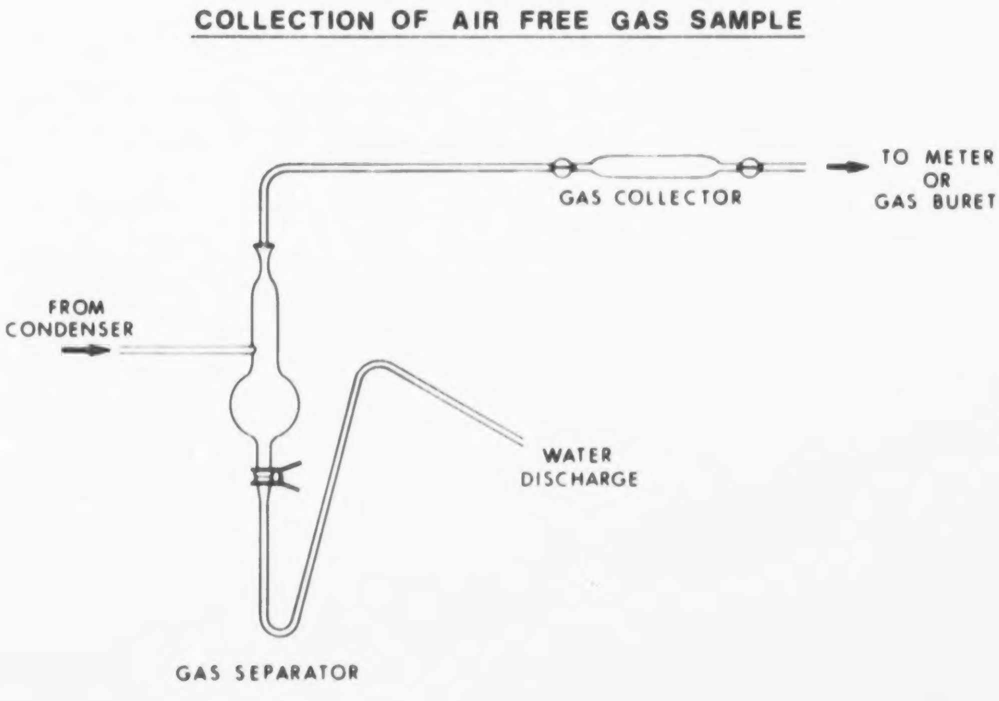
COLLECTION OF AIR FREE GAS SAMPLE
GAS COLLECTOR
TO METER OR GAS BURET
FROM CONDENSER
WATER DISCHARGE
GAS SEPARATOR

FIG. 5 - Analytical Methods - Summary

ANALYTICAL METHODS

NON-CONDENSIBLE GASES - MASS SPECTROMETRY

AMMONIA - DISTILLATION

HYDROGEN SULFIDE - IODIMETRIC

CARBON DIOXIDE - ACID EVOLUTION

FIG. 6 - Baca, N.M., Steam Well

FIG. 7 - Sample Truck & Gear

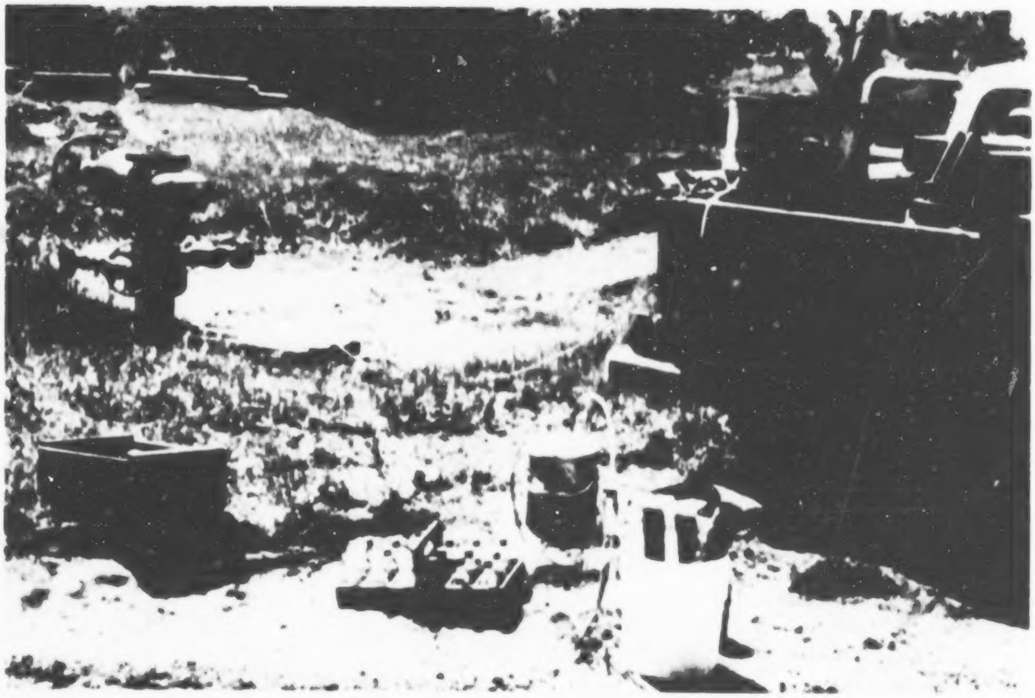

FIG. 8 - Field Laboratory at Big Geysers

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Atmospheric Discharge Sampling While Drilling Geothermal Steam Wells

by M. H. Hyman and G. R. Fox, Frederiksen
Engineering Co., Consultants, Oakland, Calif.

Presented at "Workshop on Sampling Geothermal Effluents"
U.S. Environmental Protection Agency
Environmental Monitoring & Support Laboratory
Las Vegas, Nevada

October 21, 1975

ABSTRACT

During the final phases of drilling live geothermal steam wells, considerable amounts of particulate (rock dust) and vapors are discharged. Abatement of particulates, gases and noise has been accomplished with water injection and utilization of centrifugal separators. A special method of sampling for particulates while drilling, even when active steam formations are encountered, has been proved to be successful. The sampling train employed is also useful for source testing of hydrogen sulfide, mercury vapor and ammonia.

ABATEMENT OF PARTICULATE EMISSIONS AND NOISE

At a depth determined by the geologist for each steam well, a switch is made by the drilling operator from drilling with mud to drilling with compressed air. Air at several hundred psig pressure is forced down into the well and helps bring up cuttings which travel (with any steam that is encountered) to the surface and then horizontally in a blooie line. The period of air drilling may be from a few days to a few weeks depending on drilling problems and how much steam is encountered. During that time, a heavy emission to the atmosphere of rock dust would occur if the blooie line were left open and the emission were not abated. However, the particulate can be easily abated by injection of water into the blooie line and the addition of a water/gas separator at the end of the blooie line. This separator also serves as a noise muffler.

Figure 1 shows how the well, blooie line and separator are connected. Currently at The Geysers area in northern California, the separator/muffler design frequently employed has a tangential inlet, thereby providing a centrifugal separation of particulate and water droplets from the steam and noncondensable gases. At some point in the blooie line the velocity of the steam and gases is similar to that in the throat of a Venturi scrubber. Thus, the blooie line, with water injection, and the muffler act similar to a Venturi scrubber with a cyclonic separator as used for industrial stack scrubbing.

Currently experiments are underway to find the best water injection point(s) in the blooie line; to determine the optimum water injection rate; to prove whether water can be recycled from the sump normally adjacent to the drilling rig. Water injection affects particulate abatement and abatement of certain gases such as hydrogen sulfide. In general, the higher the water rate, the better the noise reduction.

PARTICULATE SAMPLING

Our first testing of a geothermal steam well to be undertaken while the well was being drilled using compressed air injection was done by EPA Method No. 5. In this method a sampling probe is inserted into the stack, and the sample is withdrawn into a small cyclone separator followed by a flat, paper-thin filter in a heated box. The filter is followed by a series of wet impingers, a dry trap, a vacuum pump and a gas flow meter. This method did not work very well, because the filter tended to plug.

More recent testing has been successful using a method similar to that of the San Francisco Bay Area Air Pollution Control District (BAAPCD). In this method the filter thimbles utilized are made of glass packed with plugs of fiberglas wool, and inserted into the inside of the stack. This type of filtering has been demonstrated to be generally non-plugging. By having the thimbles in the stack, we are assured that the filtering is occurring at stack conditions of temperature and moisture content. Figure 2 shows a sampling train assembly that can be used.

Achieving isokinetic sampling conditions with a cyclonic separator/muffler is very difficult. Ideal isokinetic conditions are where the velocity of the gases rising in the stack is equal to the velocity entering the sampling nozzle, which is oriented to face upstream against the gas flow. However, when a cyclonic separator is employed the gas has a spiral flow pattern. Therefore, we have suggested to one of the well developers at The Geysers area that their new separator/muffler design includes straightening vanes within the stack. If this installation is accomplished accordingly, subsequent tests will show whether the velocity of the gases in the stack can be monitered more accurately. If so, the rate of sampling can then be adjusted to match the stack velocity at each point in the stack where the sample probe is inserted.

SEPARATOR/MUFFLER DESIGN

The first separator/muffler utilized had a main body diameter of 7 feet. This proved inadequate for wells discharging hundreds of thousands of pounds per hour of steam, and entrainment of mud droplets out the top of the stack was very heavy. Recent designs, using a 10-foot main body diameter, are proving to be very good for de-entrainment for the wells most recently tested.

In the design of separator/mufflers, consideration also has to be given to the ability to dismantle and easily move the apparatus from well to well as the drilling of new steam wells progresses. The separator/muffler also has to have provisions for resisting erosion caused by fast-flowing steam and rock dust. The worst wear points should have extra thick steel. Provisions should also be made for keeping the separator/muffler clean, since drilling mud is sticky and tends to build up. Normally if sufficient quantities are always injected into the blooie line while drilling is in process, the apparatus will stay clean on the inside. If the water injection is interrupted from time to time, then it is advisable to have a second source of water injected into the bottom area of the separator/muffler.

SAMPLING OF GASES AND OTHER CONSTITUENTS

In some wells, in addition to particulate sampling we have sampled for organic vapors, hydrogen sulfide and radionuclides. Forthcoming tests are scheduled for sampling gas phase emissions for ammonia and mercury vapor, with particulate to be analyzed for arsenic, lead, cadmium and sulfate. The condensate collected in the impingers will be analyzed in our lab for ammonia, bicarbonate, sulfates, chlorides, nitrates, calcium, magnesium, sodium, potassium, boron, sulfide, fluoride, iron, silicon dioxide, mercury, aluminum and conductance.

Gases such as hydrogen sulfide, ammonia and mercury vapor can be sampled directly into impingers as shown in part of Figure 2, by partially filling the impingers with the appropriate chemical reagent solutions. Organic vapors and radionuclides are normally sampled into stainless steel tanks.

CONSULTANTS

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About the Authors

M. H. Hyman has been Technical Director for Frederiksen Engineering Co., Consultants, Oakland, California since 1969, specializing in plant design, pollution control, testing, and computer applications. He previously had fifteen years of engineering experience in industry. He received a B.S. in Applied Chemistry from Caltech in 1952 and an M.S. in Chemical Engineering from the University of California (Berkeley) in 1967. He lectures at local colleges to engineers on pollution control and on computer applications, and until recently broadcasted a regular FM series on environmental technology. Mr. Hyman is registered as a chemical engineer and as a mechanical engineer and is a member of the American Institute of Chemical Engineers, American Chemical Society, National Society of Professional Engineers, and several air and water pollution control associations.

G. R. Fox is Chief Process Engineer for Frederiksen Engineering where he has been responsible for process design, environmental control, safety and corrosion problems since 1971. He previously had 12 years experience in the oil refining industry. Mr. Fox received his B.S. degree from Washington State University in 1959, and is a member of the Western Gas Processor & Oil Refiners Association.

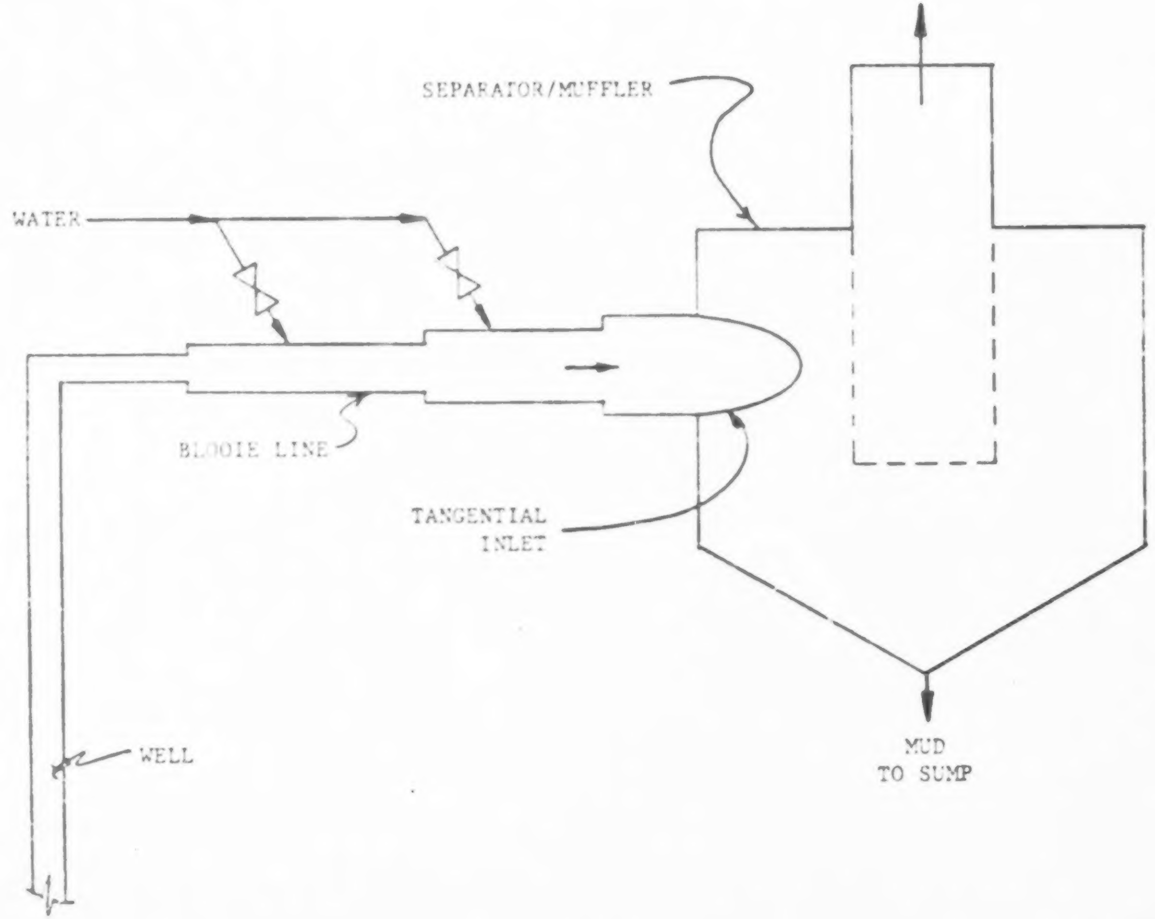
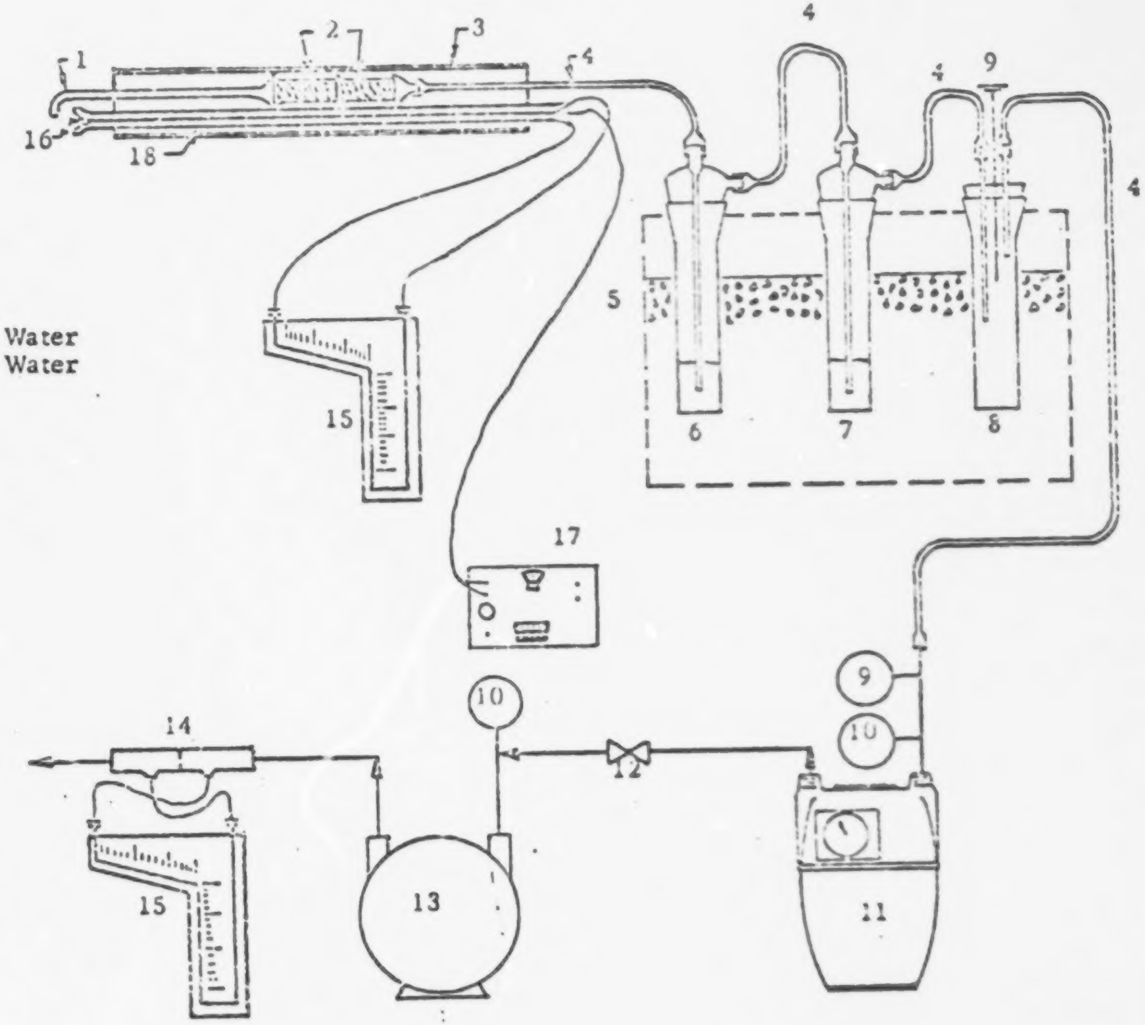

SEPARATOR/MUFFLER
WATER
BLOOIE LINE
TANGENTIAL INLET
WELL
MUD TO SUMP

FIGURE 1

FREDERIKSEN
ENGINEERING CO INC
OAKLAND CALIFORNIA

1. Nozzle
2. Fiberglass Packed Thimble
3. Probe
4. Flexible Sample Line
5. Ice Bath
6. Impinger with 100 ml Distilled Water
7. Impinger with 100 ml Distilled Water
8. Impinger, Dry
9. Thermometer
10. Vacuum Gauge
11. Dry Test Meter
12. Control Valve
13. Air Tight Vacuum Pump
14. Calibrated Orifice
15. Manometer, Inclined
16. Thermocouple
17. Potentiometer
18. "S" Type Pitot Tube



Particulate Sampling Train

FIGURE 2

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SAMPLING A TWO-PHASE GEOTHERMAL BRINE FLOW FOR CHEMICAL ANALYSIS*

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ABSTRACT

This report describes an experiment designed primarily to define the problems associated with sampling the two-phase flow in a pipeline of geothermal brine. Analyses reported for 26 samples include chemical composition, oxidation potential, pH, density, and total solids. Changes in brine composition as the well operated during a four-week period are evaluated. The apparatus and techniques used for sampling are described and evaluated.

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INTRODUCTION

When hot, highly saline, geothermal brines are used to generate electrical power, corrosion and scaling cause serious problems. Because we must understand brine chemistry to solve these problems, reliable techniques are needed for sampling and analyzing the brine.

At Sinclair #4 well, brine is produced by a flashing mechanism which gives a two-phase flow in the brine pipeline. As shown in Fig. 1, several such systems could exist. At the time this sampling experiment was designed, it was not known which system predominated. Subsequent observations, made through a sight glass on a two-inch line,[1] indicate that there is probably a boundary between the two phases but that the "liquid" phase contains entrained bubbles of vapor and the "vapor" phase contains entrained drops of liquid.

This report describes a sampling experiment conducted at Sinclair #4 well in April 1975. Its purpose was to define the sampling problems, to evaluate the reliability of samples taken from the pipeline, and to develop sampling apparatus and techniques.

SAMPLING

Samples were taken from the 6-inch line about 25 feet downstream from the wellhead using a sample probe as shown in Fig. 2. This probe was inserted into the brine stream through a one-inch valve on top of the pipeline. The tip of the probe was positioned approximately 3/4 inch below the top of the pipe to obtain top ("vapor" phase) samples and about 3/4 inch above the bottom of the pipe to obtain bottom ("liquid" phase) samples.

One-liter stainless steel sample bottles were used to collect the samples. The bottles were coated with Teflon on the inside to minimize contact of the brine with the steel. Bellows-sealed stainless steel valves were used to obtain a gas-tight seal on the bottles. A pressure gauge and throttling valve were connected to the outlet of each sample bottle to control the pressure drop through the apparatus. All bottles were flushed with N_2 prior to sampling.

Sinclair #4 well was started up on March 31, 1975. So as to permit stabilization of flow conditions, the first samples were not taken until April 3. Two samples were taken with the full flow of the 6" line discharging into the brine pond. The other samples, consisting of three sets of eight samples each, were taken at weekly intervals with the well under restricted flow to investigate the effect of four sampling parameters. The sample numbers are coded to these parameters as follows:

Date of Sampling: 6" - Samples taken April 3, 1975
1 - Samples taken April 9, 1975
2 - Samples taken April 14, 1975
3 - Samples taken April 23, 1975

Position of the probe in the pipe: T - Top
B - Bottom

Effect of cooling: H - Sample was valved off while hot
C - Sample was quenched with water

Orientation of the sample bottle: S - Bottle was sideways (horizontal)
U - Bottle was upright (vertical)

Thus, sample number 1THS denotes a sample taken on April 9 from the top of the pipe with the bottle oriented sideways (lying horizontally) and valved off hot. The well operating conditions during sampling were as follows:

Date	Wellhead P (psig)	Wellhead T (°C)	Flow
4-3-75	220	210	6" full flow
4-9-75	430	239	2" bypass line
			1/2" nozzle - 1°
			1/2" nozzle-std.
4-14-75	440	247	2" bypass line
			1/2" nozzle-std.
			1/2" orifice
4-23-75	445	255	2" bypass line
			1/2" nozzle-std.
			3/4" orifice

During sampling, the throttle valve was adjusted to maintain a 10-lb. pressure drop from the pipeline to the outlet of the sample bottle. Bottles were flushed for at least three minutes before sampling to remove residual brine from the probe and N_2 gas from the sample bottles. For samples which were quenched, the outlet valve was closed and the bottle was flooded with running water from a 3/4 inch hose for 30 seconds before the inlet valve was closed. On samples taken hot, the outlet valve was closed first and the inlet valve was closed immediately afterward.

ANALYSIS

All samples were cooled to ambient temperature and returned to the laboratory for analysis. When the samples cooled, insoluble components were precipitated out of the solution to give a three phase system. Each of these phases was analyzed separately so that the composition of the "whole" sample could be reconstructed.

Physical and Instrumental

Instrumental measurements were made on the samples before the phases were separated. Also, some physical measurements were made on the brine solutions only. Results for these measurements are shown in Table 1.

The volume of the liquid phase was obtained by dividing the weight of the liquid by the density. The weight of the liquid was taken as the difference between the weights of the sample bottle full and empty. The estimated accuracy of this measurement is ±10 cm^3.

The volume of the gas phase is the difference between the volume of the liquid phase and the volume of the sample bottle. The estimated accuracy for the volume of the gas phase is ±15 cm^3.

The measurements of pressure, pH, and E_h (oxidation potential) were obtained using a pressure cell attached to the sample bottle. This cell was a stainless steel unit fitted with a 0-200 psia pressure gauge and with ports to admit high-pressure pH and E_h electrodes. The cell was first attached to the sample bottle and flushed with argon. The sample solution was then admitted into the cell, and the pressure, pH, and E_h were measured at ambient temperature (22°C). The pressures given in Table 1 have been corrected for the volume of the pressure cell and its argon content. The estimated accuracy of these results is ±0.5 psi.

The pH and E_h measurements were obtained with a Beckman pH meter and with high-pressure (150 psi) electrodes. The pH electrodes were calibrated in standard buffer solutions prior to each measurement.

The E_h electrodes were calibrated with a Fe^{+2}/Fe^{+3} solution with a known oxidation potential.[2] The E_h valves given in Table 1 were measured with a saturated calomel electrode and corrected to the standard hydrogen potential. The negative voltage indicates a reducing condition in the solution. The spread in the values is probably caused, at least partially, by reactions between the brine and the sample bottle at points where the Teflon lining failed.

The density of the liquid was obtained by weighing an aliquot. The accuracy of this determination is ±1% of the value.

The total solids content of the samples was determined by evaporating an aliquot of the liquid to dryness at 110°C in ambient air. The reproducibility of this determination is ±5% of the value or better.

The results for the volume of solution in the top samples taken hot indicate that water vapor condensed in these samples while the bottles were being flushed with brine. As calculated from data given in the steam tables, the maximum amount of water which could exist as vapor in a one-liter bottle at 240°C and 440 psi is less than 20 cm^3 (liquid). The maximum amount of "liquid" phase brine present is less than 40 cm^3, as calculated from the total solids content of sample 1THS. (For this calculation, it is assumed that the total solids content of the bottom samples represents the total solids content of the "liquid" phase.) Thus, the maximum volume of solution in the hot top samples would be less than 60 cm^3 if vapor did not condense when the bottles were flushed. Therefore, the minimum amount of vapor condensed when the bottles were flushed ranges from 10 cm^3 on sample 1THU to 190 cm^3 on sample 1THS. Similar quantities of vapor probably condensed in the quenched top samples when they were flushed. However, for these samples, there is no way to distinguish between vapor which condensed when the bottles were flushed, and vapor subsequently condensed by quenching.

During bottom sampling, the concentration of total solids could be increased by flashing of brine or decreased by condensation of vapor in the apparatus. Because the pressure drop through the apparatus was held to 10 psi for each sample, flashing was minimized. Since it has been shown above that vapor did condense in the top samples, condensation probably predominated over flashing in the bottom samples. The amount of condensation would depend on the liquid/vapor ratio at the tip of the probe during sampling. Thus, much of the spread in the results obtained for total solids on these samples is probably caused by condensation. The average solids content for 12 bottom samples taken under restricted flow conditions is 289 g/l with a range of 40 g/l. Or, if the value for sample 3BHS is omitted, the average is 291 g/l with a range of 20 g/l. Considering that four different sampling techniques are involved, this is very good reproducibility. Also, the good agreement between the solids content of the hot and quenched samples indicates that there was not much vapor entrained in the "liquid" phase of the brine. Therefore, the higher values shown for total solids content in the bottom samples are probably very close to the true values for the "liquid" phase of the brine.

The data shown for the density and total solids content of the 1,2,3 series of samples indicates that the top samples taken with the flow restricted are primarily "vapor" phase samples while the bottom samples are primarily "liquid" phase samples. The corresponding data shown for the two samples (6"THS and 6"BHS) taken from the line under full flow conditions indicates either that the two phases were well mixed or that the top sample was taken when a slug of "liquid" phase passed the sample probe. The total solids content shown for the 6"THS and 6"BHS samples is marginally higher than corresponding values for the bottom samples from the other three sets. This could indicate a small change in brine composition as the well stabilized and flow conditions changed. However, it is more probable that the higher total solids content in 6"THS and 6"BHS occurred because the vapor/liquid ratio in the brine was higher under full flow conditions than under restricted flow conditions. The 6"THS and 6"BHS samples (full flow) were taken at 220 psig and 210°C while the other three sets of samples (restricted flow) were taken at about 440 psig and 245°C. More of the brine would tend to vaporize at the lower pressure, causing enrichment of solids in the liquid phase. If this is the case, the liquid phase nature of sample 6"THS indicates that there was slug flow in the pipeline under full flow conditions.

Carbon Dioxide and Sulfur

After the instrumental measurements were made, samples of the gas phase were taken for mass spectrometric analysis. Analyses for three samples are given in Table 2.

The CO_2 and H_2S in the gas phase were determined by sweeping the gases from the sample bottles into an analytical train with argon. The CO_2 was collected on ascarite and weighed as CO_2. The H_2S was reacted with $Pb(C_2H_3O_2)O_2$ solution and weighed as PbS. Only five samples contained detectable amounts of S as H_2S in the gas phase as shown in Table 3.

Aliquots of the solution were acidified to release CO_2 and H_2S by the following reactions.

$$CO_3^{=} + H^+ = HCO_3^-$$

$$HCO_3^- + H^+ = H_2CO_3$$

$$H_2CO_3 = H_2O + CO_2$$

$$S^{=} + H^+ = HS^-$$

$$HS^- + H^+ = H_2S$$

The CO_2 and H_2S were swept into the analytical train and analyzed as above. The H_2S content for each liquid-phase sample was less than the detection limit (0.13 mg S/ml) for the method.

Precipitates from the samples were analyzed for total S by a combustion technique.

The total CO_2 and total S assays for each sample were calculated by combining the values obtained for the gas, liquid, and solid phases. Results are shown in Table 3.

It is possible for some free S to be present in these samples. However, the reducing nature of the samples indicates that most of the S should be in the sulfide form (H_2S, HS^-, $S^=$, or metal sulfide). Thus, the results for S shown in Table 3 probably indicate sulfide sulfur. Unfortunately, portions of the Teflon coating peeled loose from the inside of the sample bottles, allowing sulfide sulfur to react with the stainless steel. Therefore, the values shown in Table 3 are probably low. The highest values should be the most nearly correct, but they could easily be in error by a factor of 2 or 3. A comparison of results for the top samples with results for the bottom samples indicates that sulfur is present in both the "vapor" and liquid phases of the brine.

The data for CO_2 indicates that most of the CO_2 is in the vapor phase of the brine as expected. The difference in concentration of CO_2 shown for the hot top samples and the quenched top samples is caused by fractionation of the CO_2, which occurred when vapor condensed during the flushing operation. In the top samples, some vapor condensed when the bottles were flushed with brine before the outlet valve was closed. Most of the CO_2 corresponding to this condensed vapor was swept out of the bottle. Thus, the CO_2 in the hot top samples includes gaseous CO_2 in the uncondensed vapor and CO_2 dissolved in the solution present when the outlet valve of the bottle was closed. In the quenched top samples, the same conditions applied until the outlet valve on the bottle was closed. Then, as the bottles were cooled by quenching, additional vapor was drawn into the sample bottle and condensed. Thus, the hot quenched samples contained additional CO_2 corresponding to the amount of vapor condensed by quenching.

Except for samples 2BHS and 2BCS, the results for CO_2 in the bottom samples are consistent. The range of these results together with the outlying values for 2BHS and 2BCS is probably caused by differences in the liquid/vapor mix encountered by the probe during sampling.

These data indicate that the concentration of gaseous constituents in either liquid- or vapor-phase samples taken from a pipeline depends on the sampling technique used and also on the extent of phase separation. It may be possible to avoid fractionation of the gases from condensed vapor by using flow-through sample bottles heated to brine temperature so that vapor does not condense when the bottles are flushed. Sampling with evacuated bottles may also prevent fractionation. Results from replicate samples will be needed to evaluate the effect of phase separation.

Cations and Anions

The salts were evaporated from two samples of brine and analyzed by spark source mass spectrometry. This method provides a qualitative multi-component analysis with approximate concentration levels. Its main purpose is to provide information concerning potential scale forming elements which may be missed otherwise. Results are shown in Tables 4a and 4b. The accuracy of the method used to analyze these samples is ± a factor of 2 times the concentration for homogenous samples. However, fractional crystallization of the salts during evaporation made these samples very heterogeneous. Therefore, these results should be used only for qualitative purposes. These results indicate that several elements such as Ni, Zn, As, Rb, Sr, and Ba should be analyzed in more detail as possible scale components. The results indicate that the concentration of most rare earths is too low for determination directly by emission spectroscopy or x-ray fluorescence without preconcentration. They can probably be determined either by one of the above techniques (if a preconcentration step is added) or directly by neutron activation.

After the phases were separated, precipitates and solutions from five samples were analyzed separately. Results are shown in Table 5.

These results indicate that the precipitates consist primarily of silica and heavy metal sulfides. The values for Ca indicate that there may also be an appreciable amount of $CaCO_3$ in the precipitates from 6" THS and 6" BHS. The accuracy of these results is ±5% of the concentration or better except for the following:

In precipitates Na, Al, Ag --- ±10%
S (as previously discussed)
In solution Ag ----------- ±10%
Al ----------- ±1.0 ppm

The results from Table 5 were used to calculate the composition of the "whole" liquid phase samples. Calculated compositions for the "whole" samples are shown in Table 6.

A comparison of the results shown for total solids by summation and by evaporation indicates that the values obtained by evaporation are biased high. This is as expected because water of hydration associated with chloride salts would not be completely removed at 110°C. However, the values obtained by evaporation are within 7% of the values obtained by summation of the elemental analyses. Therefore, the evaporative technique can be used to give a quick determination of the approximate total solids content for Sinclair #4 brine.

DISCUSSION

Under ideal sampling conditions, the liquid and vapor phases of the flowing brine would be either well mixed so that a sample would be truly representative of the whole brine or well separated so that representative samples could be taken from both the liquid and vapor phases. Our observations through a sight glass indicate that this is not the case in a pipeline where the brine is produced by a flashing mechanism. A comparison of the data for two samples taken from the 6-inch line under full flow conditions with data for 24 samples taken under restricted flow conditions indicates that the extent of phase separation is dependent on flow conditions.

Results for the total solids content of 12 samples taken from the liquid phase of the brine showed good reproducibility. The solids content of these samples seems to be independent of the sampling techniques used. These data indicate that samples taken from the liquid phase of the brine under restricted flow conditions are adequate for the determination of solid constituents.

Results for gaseous constituents indicate that the gaseous content of the samples is dependent both on the technique used to collect the samples and on the extent of phase separation. Adequate results can probably be obtained from samples taken under restricted flow conditions, if fractionation of the gaseous constituents is avoided and if replicate samples are taken so that the effect of phase separation can be evaluated. In addition, reliable results for H_2S or total S will require the development of a sample bottle that will not react with H_2S and that will serve at temperatures above 250°C and pressures above 450 psi.

Nonreactive sample bottles are also needed to take samples for the determination of E_h and pH. However, reasonably reliable results for these values can probably be obtained using stainless steel sample bottles, if the samples are analyzed immediately after they are taken.

The results of this investigation indicate that samples which are adequate for most purposes can probably be taken from pipelines where there is a definite boundary between the two phases of brine, even though the phases are not completely separated. However, the extent of phase separation is probably dependent on operating conditions. Also, the extent of phase separation has a significant effect on sample reproducibility. It would therefore be advantageous to take samples from a steam separator whenever possible.

Acknowledgments

This report is a result of the efforts of many participants. In particular, we wish to acknowledge the contributions of H. DeCoursey, R. G. Grogan, J. P. Mahler, E. S. Peck, W. E. Sunderland and M. C. Waggoner.

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Table 1. Physical and instrumental analyses.

Sample number	Soln. vol. (cm^3)	Gas vol. (cm^3)	Pressure (psia)	p^H	E_h (volts vs. Std. H)	Total solids by evaporation - 110°C (g/l)	Density (g/cm^3)
6"THS	600	380	6.8	5.1	+0.18	300	1.19
6"BHS	830	150	6.4	5.3	+0.18	325	1.20
1THS	250	730	14	5.3	+0.19	11	1.01
1THU	70	910	14	5.6	+0.16	11	1.00
1TCS	430	550	112	5.3	+0.24	2.9	1.00
1TCU	420	560	198	5.0	+0.07	3.0	1.00
2THS	200	780	10.5	--	+0.19	3.3	1.00
2THU	250	730	11.0	5.4	+0.28	1.2	1.00
2TCS	390	590	91	5.3	+0.17	0.9	1.00
2TCU	370	610	85	5.1	+0.17	0.7	1.00
3THS	170	810	11.0	5.7	+0.16	3.6	1.00
3THU	170	810	11.5	5.7	+0.08	4.0	1.00
3TCS	350	630	86	5.3	-0.08	6.2	1.00
3TCU	480	500	152	5.9	-0.03	0.8	1.00
1BHS	860	120	6.4	5.6	+0.13	290	1.18
1BHU	870	110	2.1	5.2	+0.17	290	1.18
1BCS	930	50	16	5.5	+0.15	300	1.18
1BCU	910	70	1.3	5.5	+0.13	290	1.18

Table 1. Physical and instrumental analyses (continued)

Sample number	Soln. vol. (cm^3)	Gas vol. (cm^3)	Pressure (psia)	p^H	E_h (volts vs. Std. H)	Total solids by evaporation - 110°C (g/1)	Density (g/cm^3)
2BHS	490	490	20	4.8	+0.26	284	1.18
2BHU	870	110	2.1	5.2	+0.18	280	1.18
2BCS	860	120	36	4.5	+0.28	300	1.18
2BCU	920	60	2.6	5.6	+0.16	300	1.18
3BHS	850	130	3.2	5.1	+0.24	260	1.18
3BHU	850	130	4.4	5.2	+0.16	290	1.18
3BCS	910	70	22	5.3	+0.35	290	1.18
3BCU	900	80	7.8	5.2	+0.16	290	1.18

Table 2. Mass spectrometric gas analysis.[a]

(Volume percent)

Sample	1TCU	2BCS	3TCU
CO_2	97.2	94.3	97.0
CH_4	1.7	3.9	1.9
N_2	0.5	0.5	0.6
H_2	0.5	0.9	0.4

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[a] Excludes H_2O vapor

Table 3. Carbon dioxide and sulfur analysis.

Sample number	Soln. wt. (g)	Soln. vol. (cm^3)	Vol. gas phase (cm^3)	Total CO_2 (g, weighed)	Total $\frac{g\ CO_2}{Kg\ liquid}$	S from H_2S gas (mg)	Total S $\frac{mg}{Kg\ liquid}$
6"THS	712	600	380	0.32	0.45	<0.01	12
6"BHS	988	830	150	0.18	0.18	<0.01	9
1THS	252	250	730	1.60	6.35	<0.01	3
1THU	70	70	910	--	--	--	3
1TCS	427	430	550	--	--	--	2
1TCU	418	420	560	16.4	39.2	<0.01	2
2THS	200	200	780	1.30	6.50	0.01	1
2THU	246	250	730	1.37	5.57	< .01	0.2
2TCS	392	390	590	10.6	27.0	0.26	--
2TCU	374	370	610	9.2	24.6	0.52	--
3THS	168	170	810	--	--	--	5
3THU	166	170	810	1.42	8.6	<0.01	9
3TCS	352	350	630	9.8	27.8	3.1	10
3TCU	478	480	500	16.8	35.1	1.8	5
1BHS	1020	860	120	--	--	--	5
1BHU	1028	870	110	0.18	0.18	<0.01	--
1BCS	1096	930	50	0.23	0.21	<0.01	10
1BCU	1075	910	70	0.23	0.21	<0.01	7

Table 3. Carbon dioxide and sulfur analysis. (continued)

Sample number	Soln. wt. (g)	Soln. vol. (cm^3)	Vol. gas phase (cm^3)	Total CO_2 (g, weighed)	Total $\frac{g\ CO_2}{Kg\ liquid}$	S from H_2S gas (mg)	Total S $\frac{mg}{Kg\ liquid}$
2BHS	578	490	490	1.60	3.27	<0.01	5
2BHU	1028	870	110	0.21	0.20	<0.01	--
2BCS	1017	860	120	1.79	1.76	<0.01	8
2BCU	1084	920	60	0.27	0.25	<0.01	6
3BHS	998	850	130	0.28	0.28	<0.01	16
3BHU	1002	850	130	0.18	0.18	<0.01	3
3BCS	1075	910	70	0.23	0.21	<0.01	8
3BCU	1064	900	80	0.43	0.40	<0.01	7

Table 4a. Composition of "liquid" phase samples by spark source mass spectography (sample no. 3BHS).[a]

1. H		26. Fe	4100 (M)[b]	51. Sb	<3	76. Os	<2
2. He		27. Co	<0.8	52. Te	≤5	77. Ir	<2
3. Li		28. Ni	1200	53. I	<2	78. Pt	<3
4. Be	<0.05	29. Cu	130	54. Xe		79. Au	<3
5. B	92	30. Zn	6100 (M)[b]	55. Cs	52	80. Hg	<3
6. C		31. Ga	<2	56. Ba	2600 (M)[b]	81. Tl	<2
7. N		32. Ge	5	57. La	20	82. Pb	500
8. O		33. As	100	58. Ce	<1	83. Bi	<3
9. F	0.8	34. Se	≤20	59. Pr	<2	84. Po	
10. Ne		35. Br	<2	60. Nd	<3	85. At	
11. Na	M[b]	36. Kr		61. Pm		86. Rn	
12. Mg	39	37. Rb	5300 (M)[b]	62. Sm	<3	87. Fr	
13. Al	0.5	38. Sr	4800 (M)[b]	63. Eu	<5	88. Ra	
14. Si	24	39. Y	<2	64. Gd	<3	89. Ac	
15. P	<0.08	40. Zr	24	65. Tb	<1	90. Th	<1
16. S	390	41. Nb	<2	66. Dy	<3	91. Pa	
17. Cl	M[b]	42. Mo	<8	67. Ho	<1	92. U	<1
18. Ar		43. Tc		68. Er	<3	93. Np	
19. K	M[b]	44. Ru	<5	69. Tm	<1	94. Pu	
20. Ca	M[b]	45. Rh	<2	70. Yb	<3	95. Am	
21. Sc	<0.5	46. Pd	≤5	71. Lu	<1	96. Cm	
22. Ti	<8	47. Ag	<3	72. Hf	<3	97. Bk	
23. V	<0.8	48. Cd	<40	73. Ta	≤8	98. Cf	
24. Cr	<8	49. In	<2	74. W	<3	99. Es	
25. Mn	7500 (M)	50. Sn	<20	75. Re	<2	100. Fm	

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[a] Results expressed in mg/l.

[b] Major constituent.

Table 4b. Composition of "liquid" phase samples by spark source mass spectrography (sample no. 4BHU).[a]

1. H		26. Fe	1000	51. Sb	<3	76. Os	<2
2. He		27. Co	<0.6	52. Te	<1	77. Ir	<1
3. Li		28. Ni	450	53. I	<2	78. Pt	<2
4. Be	0.15	29. Cu	45	54. Xe		79. Au	<2
5. B	140	30. Zn	2200	55. Cs	20	80. Hg	<3
6. C		31. Ga	<1	56. Ba	3000 (M)[b]	81. Tl	<1
7. N		32. Ge	3	57. La	15	82. Pb	450
8. O		33. As	2700	58. Ce	<1	83. Bi	<2
9. F	2	34. Se	6	59. Pr	<2	84. Po	
10. Ne		35. Br	<2	60. Nd	<2	85. At	
11. Na	M[b]	36. Kr		61. Pm		86. Rn	
12. Mg	27	37. Rb	120	62. Sm	<2	87. Fr	
13. Al	1	38. Sr	3700 (M)[b]	63. Eu	<3	88. Ra	
14. Si	9	39. Y	<1	64. Gd	<3	89. Ac	
15. P	0.6	40. Zr	6	65. Tb	<1	90. Th	<1
16. S	270	41. Nb	<1	66. Dy	<2	91. Pa	
17. Cl	M[b]	42. Mo	<6	67. Ho	<1	92. U	<1
18. Ar		43. Tc		68. Er	<2	93. Np	
19. K	M[b]	44. Ru	<1	69. Tm	<1	94. Pu	
20. Ca	M[b]	45. Rh	<1	70. Yb	<2	95. Am	
21. Sc	<0.6	46. Pd	<2	71. Lu	<1	96. Cm	
22. Ti	<6	47. Ag	3	72. Hf	6	97. Bk	
23. V	<0.6	48. Cd	9	73. Ta	≤6	98. Cf	
24. Cr	<6	49. In	<1	74. W	<2	99. Es	
25. Mn	1900	50. Sn	<15	75. Re	<1	100. Fm	

[a] Results expressed in mg/l.

[b] Major constituent.

Table 5. Liquid-phase samples (analysis of precipitates and solutions).

	Precipitates						Solutions				
Sample	1BHS	2BHS	3BHU	6"BHS	6"THS	Sample	1BHS	2BHS	3BHU	6"BHS	6"THS
Wt. of ppt (mg)	680	315	503	896	647	Vol. of soln. (cm^3)	864	485	849	826	598
	Analysis (wt. %)						Analysis (mg/l)				
Na	0.04	0.03	0.04	0.02	0.05		64000	61000	70000	74000	64000
Mg	0.09	0.12	0.05	0.26	0.23		72	70	71	77	74
Al	0.06	0.08	<0.01	0.14	0.14		2.2	1.7	2.1	1.7	3.2
Si	27.9	28.8	34.8	21.5	21.9		37	47	42	44	40
S	0.82	0.93	0.61	1.03	1.32		<0.2	<0.2	<0.2	<0.2	<0.2
Cl	-	-	-	-	-		166000	161000	165000	185000	179000
K	0.32	0.24	0.38	0.28	0.34		15300	14000	15800	16700	[illegible]700
Ca	0.55	0.15	0.08	5.59	3.83		28700	28200	29000	31500	[illegible]0400
Mn	0.44	0.07	0.04	0.42	0.54		1200	1180	1220	1330	1300
Fe	9.36	6.33	1.31	11.4	11.4		1410	1440	1440	1430	1470
Cu	0.38	0.47	0.27	0.38	0.21		0.95	0.80	1.08	2.06	1.02
Ag	0.001	0.001	0.001	0.001	0.002		0.7	0.6	0.5	0.7	0.7
Pb	0.29	4.32	0.12	0.14	0.51		99	63	101	107	105

Table 6. Liquid-phase samples (reconstructed analysis).[a]

Element	6"THS	6"BHS	1BHS	2BHS	3BHU
Na	64000 mg/l	74000 mg/l	64000 mg/l	61000 mg/l	70000 mg/l
Mg	76	80	90	71	71
Al	5	3	2	2	2
Si	278	277	257	234	249
S	14	11	6	6	4
Cl	179000	185000	166000	161000	165000
K	14700	16700	15300	14000	15800
Ca	30400	31500	28700	28200	29000
Mn	1310	1340	1200	1180	1230
Fe	1600	1550	1490	1490	1450
Cu	3.3	6.2	3.9	3.9	2.7
Pb	111	110	102	92	101
Ag	0.7	0.7	0.7	0.6	0.5
Total Solids (g/l) by Summation	291	310	277	267	283
Total Solids by Evaporation (g/l)	300	325	290	284	290
Date	4-3-75	4-3-75	4-9-75	4-14-75	4-23-75
Temperature (°C)	210	210	239	247	255
Pressure (psig)	220	220	430	440	445

The difference in operating conditions probably caused the values for total solids shown for 6"THS and 6"BHS to be higher than values for the other three samples. More brine would tend to vaporize at the lower pressure, causing enrichment of solids in the liquid phase of the brine.

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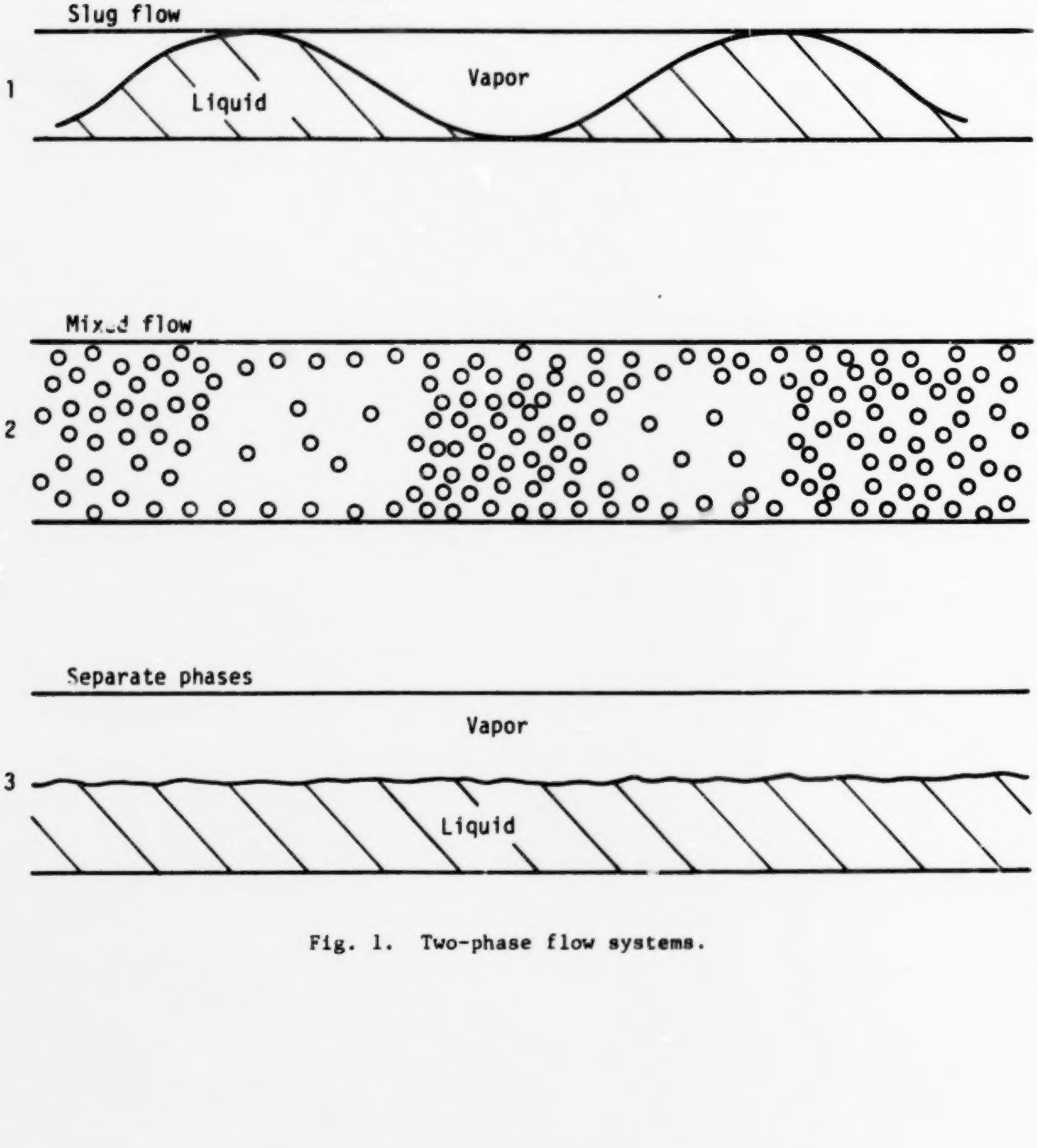
[a] Calculated from values in Table 5. These values indicate the composition of the whole "liquid" phase sample.


Slug flow
1
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2
Separate phases
Vapor
3
Liquid

Fig. 1. Two-phase flow systems.

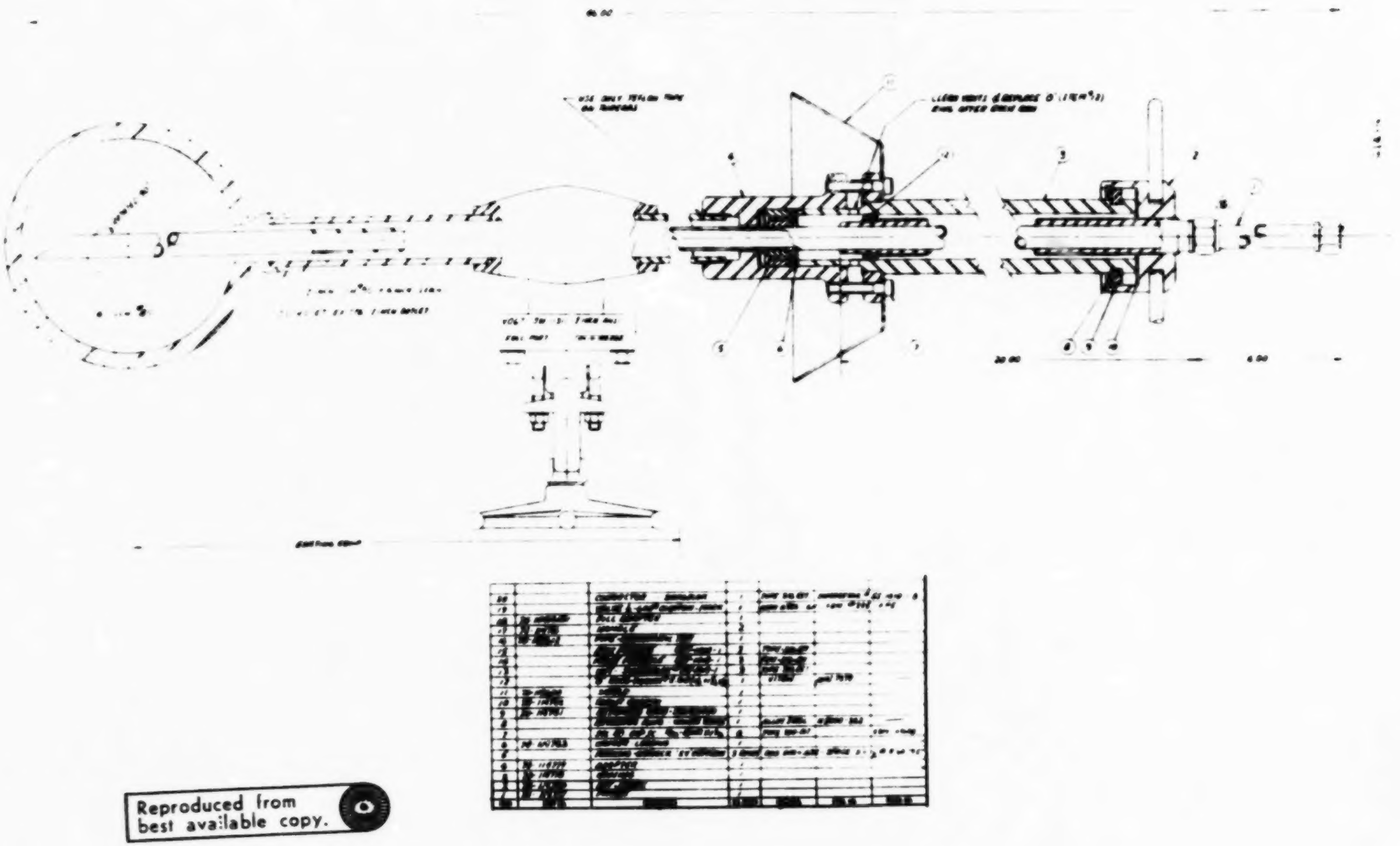
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Fig. 2. Sampling probe.

APPROACHES TO INTERPRETING ENVIRONMENTAL DATA

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INTRODUCTION

The sampling of geothermal effluents presents many intriguing challenges, but in the end the question will be asked, "What does the data mean?" Does it provide a basis for legal prosecution or defense?, does it portend detriment to some biological entity?, does it provide grist for intellectual endeavor? or is it merely another set of numbers in a report destined for oblivion?

Oblivion is deserved when the sampling fails to correspond in a logical way with either suspected or actual features of an environmental pattern. The notion of pattern in space or time is crucial to the setup of any sampling procedure. It is the meager attention sometimes given to patterns that prompts this presentation.

The four topics discussed below (superimposed dispersion patterns, regionalized variables, risk assessment and concepts of impact) at first seem disconnected, but upon closer reflection can be seen to have a common underpinning. Namely, they concern the question, "how can an obscure but non-random dispersion pattern be coped with in the taking of samples and in using data to convey ideas about environmental conditions? The first two of these topics are statistical but of a viewpoint not commonly used in the U.S.. The next concerns the mismatch between real environmental inventories of contaminants and quantities that are advertised as dangerous. The last shows that the scale of pattern we are interested in will determine the very definition of environmental impact we might construct.

These comments are more general than the geothermal context of this meeting. They are stirred by a hope that regulatory objectives now being formed will be both fair in the legal sense and astute with respect to physical fact.

Controversy becomes very heated when environmental data is used differently by opposing factions in an issue. Much of the heat is counterproductive; environmental data should be recognized as ambiguous, especially in small quantities. As professionals, one goal is to minimize these ambiguities. It is with that motive also that the following ideas are presented.

SUPERIMPOSED DISPERSION PATTERNS

A fundamental problem in environmental monitoring is to decide whether or how much effluent has reached a particular environmental compartment. The two facets of this problem concern: (1) what geographical extent of the compartment should be sampled, and (2) how does effluent material detected by analysis relate to a postulated source? Empiricism is required for both. Analysis of statistical distributions has been useful in some cases to answer both facets simultaneously.

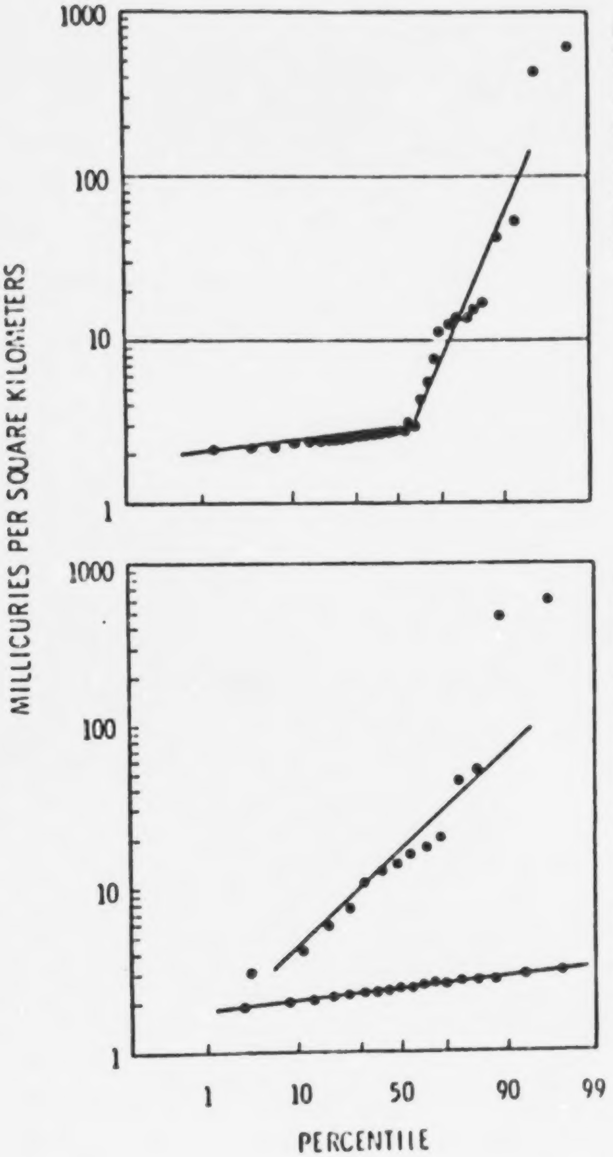
If we consider for a moment a set of samples whose contaminant content is dominated by a single source, the distribution of values can be characterized by a mean (geometric) concentration and a standard (geometric) deviation. (The adjective "geometric" is appropriate for log-normal distributions.) Both the mean and the standard deviation are unique attributes of the source via the dispersion mechanism. More generally, a point source of contaminant will decorate an environmental compartment unevenly with the result that the contaminant contents in some places will be dominated by the point source, and in others by factors we call background. The cases where background and effluent levels are comparable in magnitude are seldom a large fraction of the affected area. Thus, the statistical problem is one of resolving superimposed distributions.

One way of attempting this resolution is diagramed in Figure 1 which is a pair of probability plots(1). The upper plot shows the whole data set considered as an entity. But because the data are not distributed about a single straight line at least one of the presumptions in making the plot does not fit physical reality. These key presumptions are:

(1) The data must come from a homogeneous (single) distribution. That is, the best descriptor of the set is a single mean value combined with a single standard deviation.

(2) The distribution type, Gaussian, log-normal, Weibull, etc., has been chosen correctly in order to properly scale the axes.

If presumption 2 were violated by the plotting, the outcome would be a curved array of plotted data rather than the sharply jointed array in the upper plot. Thus, we test instead for two superimposed log-normal distributions. This is done by dividing the data into two groups, recomputing percentiles, and replotting as in the lower plot. There are several ways to judge whether the division of data, as done, leads to a good way of describing physical reality. The smaller sub-set in this case did conform to actual estimates of a background distribution and the excellent linearity shows that at least the data assigned are statistically homogeneous. Furthermore, checking the sample locations for all the samples in the higher value sub-set showed that on a map they could be separated from the background set with a single simple line. That is, they are geographically correlated as well as statistically correlated. One could have bypassed the statistics and drawn a line on a map of sample locations, outlining the area which contained the high samples and the result would have been largely correct. The advantage of using also the statistical plot lies in



A
THE JOINTED LINE THROUGH THE PLOTTED DATA INDICATES TWO DISTRIBUTIONAL MODES. THE POSSIBILITY IS REALISTIC IN CONCEPT SINCE THE SOILS WERE SAMPLED BECAUSE OF A SUSPECTED CONTAMINATION ZONE, HENCE SOME MUST REPRESENT BACKGROUND.

B.
SAME DATA AS IN (A) BUT WITH PERCENTILES REASSIGNED ASSUMING A MIXED DISTRIBUTION WITH LITTLE OVERLAP

THE LOWER VALUE DISTRIBUTION CAN BE INTERPRETED AS BACKGROUND. THE FACT OF CONTAMINATION IS EVIDENCED BY PRESENCE OF A DISTRIBUTION MODE THAT IS DISTINCT FROM BACKGROUND.

GEOGRAPHICAL LIMITS OF THE CONTAMINATION CAN BE MAPPED BY REFERENCING THE SITES IDENTIFIED BY THE TWO DISTRIBUTIONS.

FIGURE 1 Separation of Mixed Distributions

reducing the number of data points that have ambiguous levels. This is one example of how to reduce subjectivity in judging which samples do not show influence of a suspected source.

ALEATORY VS. REGIONALIZED VARIABLES

Classical statistics concerns variables which have two properties that are exemplified by the flipped coin. (1) the variable can be determined an infinite number of times, at least in principle and (2) the outcome of one determination is not functionally related to the outcome of another determination of the same kind.

Those two properties are generally absent in environmental situations. That is, the effluent material in a single sample is unique in the sense that the identical amount of effluent should not be expected in a repeat sample. Note also that the repeat sample involves a different portion of the medium. Furthermore, the analytical results of multiple environmental samples taken closely together would be more nearly alike than the analytical results of similar samples taken over a broader spacing. That is, the outcomes of the individual measures are not independent in the aleatory sense. Because classical statistical tests are based on concepts of randomness and independence, the results of those tests should be interpreted with caution in regards to environmental dispersions.

Regionalized Variable

In the last two decades mining engineers and geologists largely from France and South Africa have developed a discipline called geostatistics(2). The focus is on ore grades and ore reserves and error estimations for those values. There are substantial parallels between dispersions of ore components and environmental contaminations. A key concept in geostatistics is the regionalized variable which (1) has a definite value at each point of space, (2) shows a more or less continuity in its spacial variation, and (3) may show different kinds of zonal effects. Generally concentration is the regionalized variable which is to be studied by measuring its value at selected points in space and time.

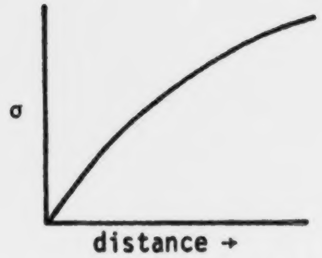
Variogram

A principal tool for investigating the regionalized variable across space is the variogram. This diagram is essentially (but not exactly) a plot of apparent standard deviation for concentration versus separation distance of samples used to compute the standard deviation. The variogram can take several forms but they all represent different degrees of continuity of concentration across space, as shown in Figure 2.

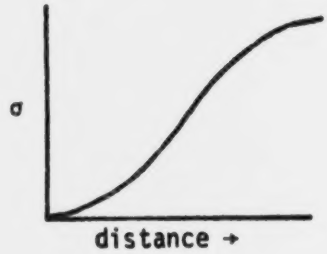
For a single dispersion it sometimes happens that different variograms apply to different directions. These situations can result either from a depositional environment which is directionally non-uniform or from a dispersion mechanism that is directionally non-uniform. Environmentally, the latter corresponds to atmospheric mixing coefficients that differ downwind, cross-wind, and vertically.

All the variograms tend toward an asymptote-like condition at large separations between samples. This brings in a concept important to both the layout of sampling nets and the interpretation of data. If the sample spacing is too small, adjacent samples are quite similar and the detail obtained for the distribution pattern may be greater than required. This kind of overdetermination is somewhat cost ineffective. On the other hand, if samples are taken at too great a spacing some of the space between samples is poorly represented by any "nearest" sample. This results in a possibility that an important occurrence may pass unnoticed.

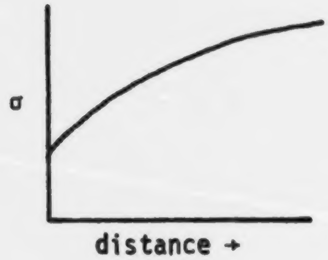
Figure 2: Types of Variograms



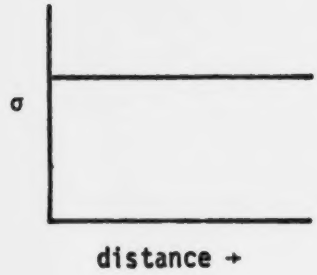
Linear: The most common; represents a simple ideal regionalized variable.



Continuous: Small variability at short range shows a high continuity, for example. The thickness of a sedimentary bed.



Nugget effect: Distribution is discontinuous in small samples, not fully conforming to the ideal regionalized variable.



Random: A limiting case corresponding to an aleatory variable.

Adapted from G. Matheron, 1963

Early in the sampling program a variogram could be constructed from preliminary data. Ideally, it would be used to set up a routine sample spacing that would be sensitive to pre-selected scale of differences between analytical values. It may turn out that sample spacing should be different in different places as well as in different directions.

This approach can be applied to the technique for taking individual samples as well as in the setup of an extensive net. For example a single scoop of soil, which physically involves only a few square inches of area may be taken to represent tens of thousands of square feet of geography. Representivity could be improved by compositing several scoops from an area of hundreds of square feet that constitute the sample site. The question arises, "how much separation between scoops?" In one situation, soil sampling for ^{137}Cs from fallout(3), several 10-cm square samples were taken and the results used to construct a variogram. It was found that samples separated by one meter had a relatively small standard deviation, whereas samples on a two-meter separation showed a larger standard deviation, about the same size as for the set as a whole. Thus, in compositing, the scoops should be separated by more than one meter, but there is not statistical advantage in having the scoops separated by more than two meters. Notice that in compositing, one goal is to submerge the small scale variability by swamping it with components that are random with respect to that small scale variability within the sample site. Contrast that goal with a main objective of a sampling program - - the taking of (composite) samples in such a way that non-random variability between sites becomes more apparent that it would be by any other sample spacing.

RISK ASSESSMENT

This issue has been contaminated by "Environmental Jitters". Some people(4) feel that scientists who encourage public fears on the basis of of incomplete or ill-digested evidence constitute a serious environmental problem. The reference (4) concerns fluorocarbon aerosol propellents and there are other examples from cyclamate to CO_2.

There is a point in the plutonium debate that seems to be seldom recognized. The same point occurs in debate about other contaminants so the intent here is not to continue the plutonium debate, but rather to show that: (1) environmental exposures with some similarity to postulated calamities have been underway for decades; they deserve to be assessed in terms of transfer coefficients between media and populations, and (2) numeric values for transfer coefficients can be estimated, at least in gross aspects from fairly general data. These estimates should serve to limit speculation about how severe a postulated event might be. Although this discussion is limited to plutonium, counterpart calculations can be made for lead, cadmium, selenium, mercury, radon etc.

Fallout from weapons testing prior to 1970, dispersed about 300,000 curies (7 tons) of Pu-239 and Pu-240^(5)^. This amount is large compared to industrial losses even in serious incidents. Our expectations about what happens to plutonium that escapes from industrial containment should be tempered by what has happened to the plutonium from weapons fallout. The behavior of the plutonium from the two kinds of sources will not be identical since, for example, the particle size distributions are not alike and the atmospheric distribution mechanisms are partly different. However, the fallout case can serve as a reference. Whether the industrial context suggests a more efficient or less efficient transfer of plutonium into people can be estimated from details about the industrial context and how they contrast with fundamentals of the fallout context.

Autopsies of people from the general public who were living throughout the major period of weapons fallout, show that they carried plutonium in amounts near an average of 5×10^{-13} curies (0.5 picocuries per person)(6). From that result, the total amount of Pu inside living people can be estimated by multiplying the average burden by the world population; (0.5 picocuries/person) times (3×10^{9} persons/world population) = 1.5×10^{-3} curies/world population.* Thus, of the entire 300,000 curies of Pu in the world environment, only about five billionths (5×10^{-9}) is actually inside people where it exposes them to alpha radioactivity. Thus, a transfer coefficient from environment to human bodies can be crudely estimated at 5×10^{-9}.**

In applying this result to the context of malcontainment of industrial plutonium we should consider three aspects of the contamination. First, is the total plutonium in an installation. Second, if a release occurs only a part of the total plutonium will actually escape into the environment before cleanup operations repackage what can be recovered. Third, of the plutonium which escapes, only a fraction will actually end up in people. It is the size of this last fraction which is of ultimate concern to human health. Whatever detriment is calculated to accrue to humanity must be based on this smallest fraction.

*Probably this gives an overestimate since the 0.5 picocurie figure is an average based mainly on persons who were alive throughout the major period of fallout from weapons. Younger people missed the major part of the fallout episode, however, measurements of the plutonium burdens have not been included in proportion to their population. Including young people in the population figures of 3×10^{9} is conservative in the sense that the results of the calculation will show more plutonium in the world population than what a more refined calculation would show.

**This value lumps the oceanic and land inventories of plutonium but the distinction is largely irrelevant if most of the population burden was acquired by inhaling primary fallout, in contrast to inhaling fallout re-entrained from soil or ingestion through the food chain.

Many scare comments about industrial effluents ignore the inefficiency by which environmental levels are carried on to people. Several statements in print say, in essence, that one ounce of plutonium can poison all the world population. Credibility of such statements seems strained since we do not appear to be seriously poisoned by the 7 tons already in the environment. Distinctions must be made, of course, between materials like DDT which increase up the food chain and those like plutonium which decrease.

More sophisticated estimates of transfer coefficients from environment to human populations can be made. Some already exist for specific conditions of soil content, reetrainment, and other aspects of environmental pathways(7). These kinds of calculations, based on simple or complex assumptions deserve to be recognized and used publicly in describing how socially important decisions could be based on environmental data. One proper goal is to counter scare comments with objective comparisons between current dispersions of contaminants and inducible changes in the patterns.

THREE CONCEPTS OF IMPACT

Part of the difficulty in laying out environmental sampling (monitoring) programs is due to obscurity of what an impact is and how one quantifies an impact by looking at data. There are three distinct ways of looking at environmental impact and they require different techniques for sampling and data interpretation. Debates about impact commonly obscure the distinctions to the detriment of resolving issues. These approaches are:

(1) Summing emissions from sources,

(2) Measuring concentrations of contaminants in air, soil, water or biota at distance from the source,

(3) Observing the biological effects due to increased levels of contaminants in parts of the ecosystem.

The third approach is of ultimate significance, of course, but conclusions about detriment are seldom timely and early observations are difficult to present in a convincing way to persons who are sceptical that the cause of an affliction has been identified. Furthermore, causes of environmentally induced afflictions are seldom singular and it is difficult to obtain agreement upon which of the causitive factors is most important, especially in a legal contest.

The second approach has value to a defensive legal posture since it can identify the geographical boundaries outside of which responsibility for effects can be denied. The results from this approach have immense academic interest to some scientific fields, but even the best work can get a "So what's new?" response from a person interested narrowly in the third approach.

The first approach is the handiest for legal applications (especially prosecution) because sampling and analytical results are the least ambiguous of all the approaches. However, it is sometimes a long environmental path between a source and a biological effect so that the precise data from the first approach risk being thoroughly irrevelant. For example, the chemical form of an effluent may have a short lifetime in the environment or the effluent may be a trivial increment to a naturally occurring background.

I have belabored the distinctions among these three approaches because the standards of good work in one approach are quite different from the counterpart standards in other approaches. Furthermore, persons who narrowly champion one approach have no logical basis for debate with a representative of another approach. Indeed, there are no reliable logical connections between the approaches except the trivial one that emission precedes dispersion which precedes biological effects. Even the principle of mass conservation applies unevenly because most effluents are changed chemically within the environment. This is to say that in only a special few cases does the integrated effluent equal the (incremental additions to) contents in environmental compartments.

CONCLUSIONS

Some persons at this meeting have commented about how individualized the sampling technique must be for different geothermal sources, even of the same type. Perhaps this is due to the obscurity of important features of basic patterns. In order to establish standard or reference procedures aimed at regulation of geothermal sources we would be well advised to first study the patterns involved. In this way, the standardized parts of a procedure could be well aimed at particular features which geothermal sources have in common in their own patterns of behavior or patterns of dispersion of their effluents. Comparability must be one of the motives behind setting up standardized procedures. Not all components of individual patterns are equally useful in comparing one geothermal source with another. We should learn which features are important to our purposes, either academic or regulatory, and then focus the standardization of sampling toward those features. The interpretation of geothermal data must begin before the samples are taken.

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Sampling and Preservation Techniques for Waters in Geysers and Hot Springs

by

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with a section on

Gas Collection

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ABSTRACT

Sampling of geothermal fluids presents unique challenges, due to the instability and wide concentration range of many constituents. Unstable parameters, such as pH, Eh, temperature and dissolved oxygen are determined on-site. Filtration of geothermal water is done with absolute minimum time-delay and exposure of the sample to air, by using a portable pump and non-contaminating, all-plastic or all-metal filter apparatus, for samples for inorganic or organic determinations, respectively. Sample preservatives and their safe, efficient transportation are discussed. Two techniques of geothermal gas collection are presented along with details of gas sampling apparatus.

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INTRODUCTION

Unique problems are encountered in the sampling, preservation and analysis of geothermal fluids because of the instability and/or high concentrations of some constituents. Silica may occur at concentrations up to several hundred milligrams per litre; therefore, silica may polymerize during sample storage and not react with molybdate color forming reagents, or precipitate, with concurrent loss of coprecipitating elements. Arsenic^{+3}, iron^{+2} and other variable valence ions may be rapidly oxidized upon aeration at elevated temperatures, precluding valence species determinations. Sulfides may be rapidly oxidized by dissolved oxygen, and hydrogen sulfide gas is unstable in the presence of moisture, oxygen, and to a lesser extent, ultraviolet light. The pH may rise rapidly (up to two orders of magnitude in our experience) due to exsolution of dissolved carbon dioxide, or decrease due to carbon dioxide uptake or hydrogen sulfide oxidation.

Due to the greater cost, and the tendency to lowered precision and accuracy, of field analyses as compared to laboratory analyses, analyses should be done on site for only those constituents which cannot be preserved for laboratory analysis. Exceptions may occur when knowledge of some parameter is needed to guide subsequent sampling, and when adequate analytical tools are available. pH, Eh, and temperature are, of course, determined on site. If necessary, carbonate-bicarbonate alkalinity can be determined later as long as the non-carbonate alkalinity is not significant and the pH is also remeasured (Ellis, et al., 1968; A. H. Truesdell, unpub. data). Alternatively, immediate alkalinity titration may be difficult because at the time of sampling even gentle stirring promotes the vigorous exsolution of supersaturated carbon dioxide resulting in pH increase (equation 1)

$$H^+ + HCO_3^- \rightleftharpoons H_2O + CO_2\uparrow \qquad 1)$$

even while acid is being added.

Due to the instability of the dissolved constituents of geothermal fluids, immediate filtration of the hot water without allowing degassing of waters supersaturated with carbon dioxide is necessary (equation 1). The high concentration of trace elements in the sinter and other surficial deposits mandates stringent precautions to avoid water sample contamination.

Methods of collection and analysis of geothermal waters have been published by Ellis, et al. (1968) and by Presser and Barnes (1974). Geothermal gas collection and analysis schemes have been described by Ellis, et al. (1968), Akeno (1973), and Giggenbach (1976). The entire field has been reviewed by Finlayson (1970).

WATER COLLECTION

ON SITE ANALYSES

Determination of pH and Eh is accomplished elegantly by pumping sample fluid (slowly for pH, rapidly for Eh) through an insulated cell (Fig. 1) containing pH, Eh and temperature probes. The probes are of rugged, high-impact plastic construction, and glass electrode membranes are well protected. Liquid junctions are of a type highly resistant to clogging and fouling, and the electrodes are usable up to and including 100°C without damage. A meter with compatible electrodes is used to measure both pH and Eh. If equipped with intercept, slope, and temperature compensation knobs, the meter may be standardized with bracketing buffer solutions at ambient temperature prior to each measurement (Sargent-Welch Scientific Co., undated). Otherwise

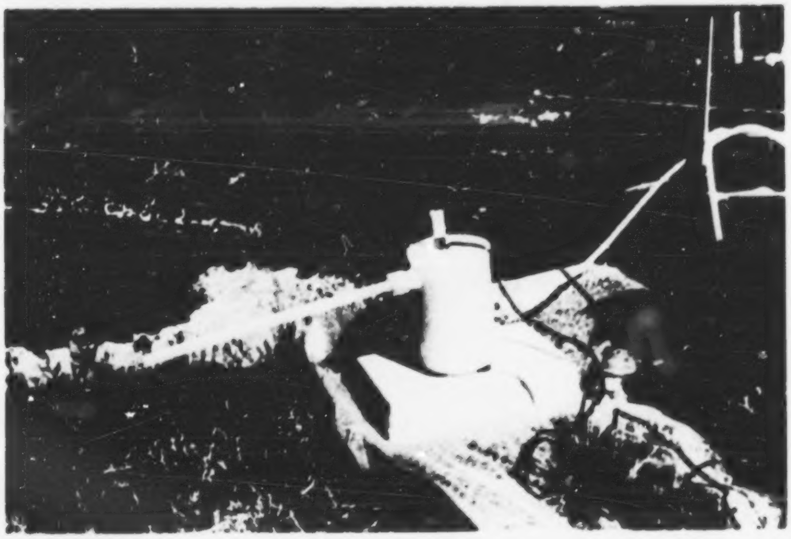

Fig. 1. Flow-through pH-Eh cell.

standardization with buffers at the sample temperature is necessary. Actual Eh values are calculated later from the EMF value, the half-cell potential of the reference cell and the temperature. The lid of the meter's carrying case (Fig. 2) serves as a sun shield to minimize temperature changes in the meter.

Dissolved oxygen is determined by modified Winkler titration; manganous sulfate and alkali-iodide-azide contained in sealed pieces of plastic tubing are added on site. The samples are thereafter kept out of direct sunlight. The sulfamic acid is added just before analysis, which is carried out as soon as possible.

SAMPLING

Due to frequent remoteness of sampling sites, compact, lightweight equipment is used which may be transported, along with the samples taken, in two backpacks (weight ≥ 20 kg each). The portable pump (Fig. 2) used to pump sample water through the flow-through pH-Eh cell and the filter apparatus, is capable of delivering the sample fluid from a depth of at least three meters to the apparatus with a head of at least 20 psig (1.4 kg/cm^2) for at least four continuous hours, the most extreme conditions encountered thus far.

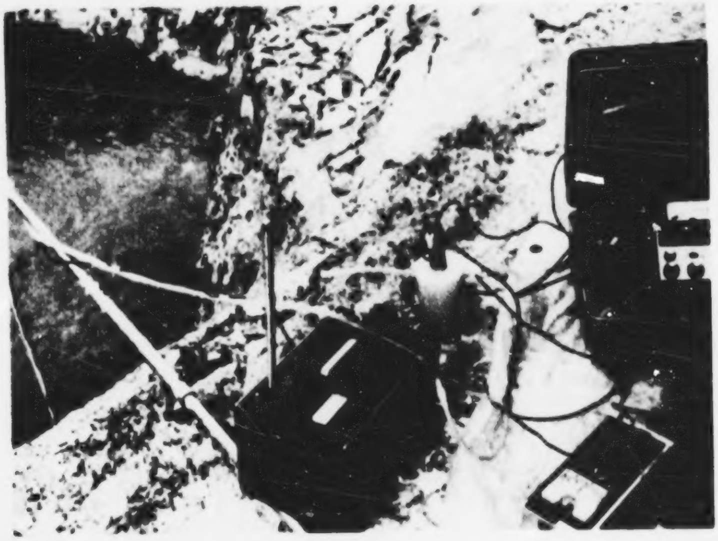

Fig. 2. Field setup, showing sampling line, portable pump, flow-through pH-Eh cell, telethermometer and pH meter.

The polyvinyl tubing through which sample water is pumped is held in place using a 2.5 cm o.d. sectioned aluminum pole having an adjustable stainless steel laboratory clamp attached to one end (Fig. 3).

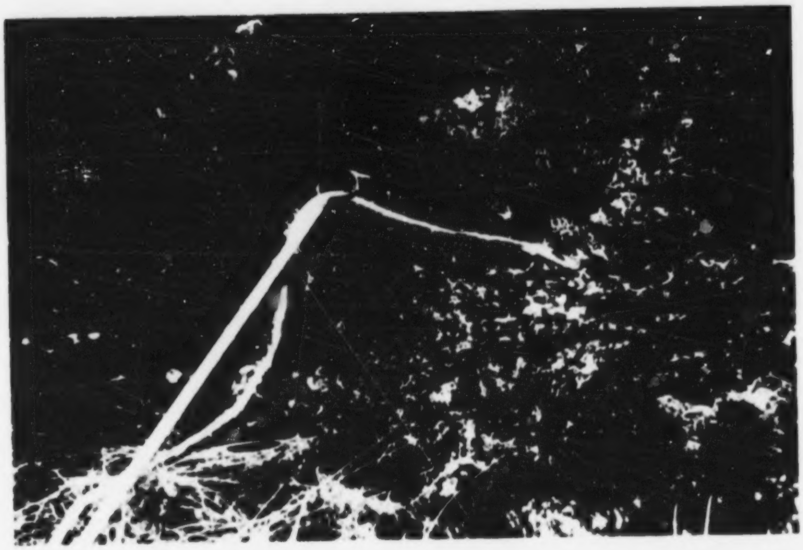

Fig. 3. Sampling line in use in hot spring overflow.

The sampling line inlet is weighted to prevent flotation of the polyvinyl tubing. The effectiveness of the pole for positioning the sample tubing over a small spouting hot spring is shown in Fig. 4.

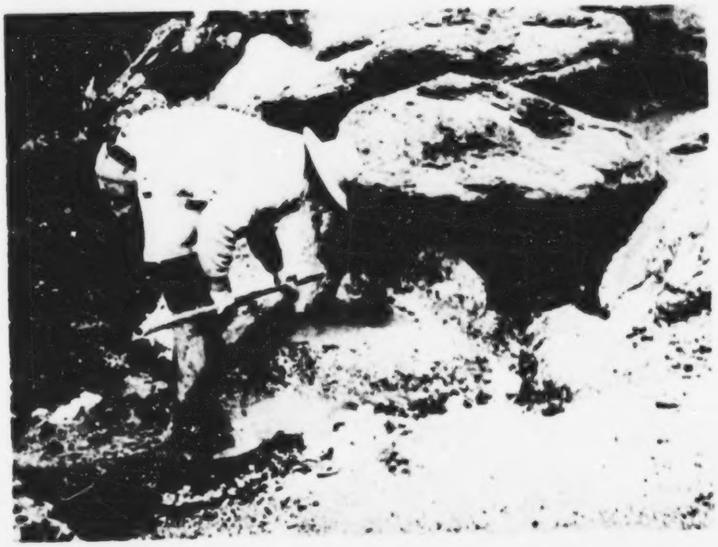

Fig. 4. Positioning the sampling line over spring.

The all-plastic filter used (Fig. 5) holds a 0.1 µm 142 mm membrane between two plexiglass discs sealed with a viton rubber o-ring; the air is released at the start of filtration using an integral valve; and the assembly is supported by three polyvinyl chloride legs threaded into the underside of the bottom disc. The two discs are secured together by integral, swing-away nylon bolts and nuts hinged in the bottom plate.

Sample fluid is pumped from the source through the filter assembly into all-polyethylene or glass collection bottles (Fig. 5). The membrane may be saved by placing it in an acid-washed petri dish. Cleaning consists of wiping the inside of the filter with tissue, rinsing with distilled water, and changing the filter membrane; sample water from the new site is used to thoroughly flush the sampling line during pH and Eh measurements; the sampling line is then attached to the filter and the membrane is flushed with 250-500 ml of sample.

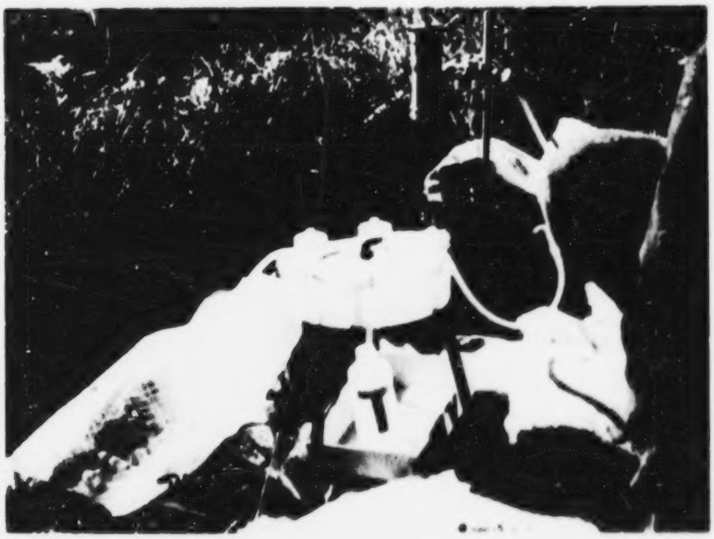

Fig. 5. Filtration assemblies.

Samples are collected after on-site analyses are completed. Samples for major cations(250 ml), major anions(500 ml), nutrients(250 ml), sulfide(250 ml), and iron 2/3 and arsenic 3/5(250 ml) are collected first; then samples for Hg; then samples for trace elements. Duplicate samples may be taken for trace constituents.

Samples for mercury determination are collected in a 250, 500 or 1000 ml borosilicate glass reagent bottle, any of which is compatible with our mercury analytical system. The mercury sample bottles are cleaned with an overnight soaking with chromic acid, rinsed five times with distilled water and oven dried at least two hours at >200°C to drive off residual mercury.

Samples to be analyzed for total dissolved organic carbon are pumped through a silver filter membrane housed in a cylindrical filter assembly of stainless steel and Teflon construction (Fig. 6) (Malcolm and Leenheer, 1973). The membrane is flushed with approximately 200 ml sample water; 30-40 ml of filtrate is then collected in a glass bottle which has been fired at 500°C for six hours and capped with fired aluminum foil (Malcolm and Leenheer, 1973).

An effective way to avoid contamination of the sample water by surrounding sinter is use of a nylon-reinforced polyethylene ground sheet. The operator and all his equipment fit on a 10-foot square sheet (Fig. 1, 2, 5).

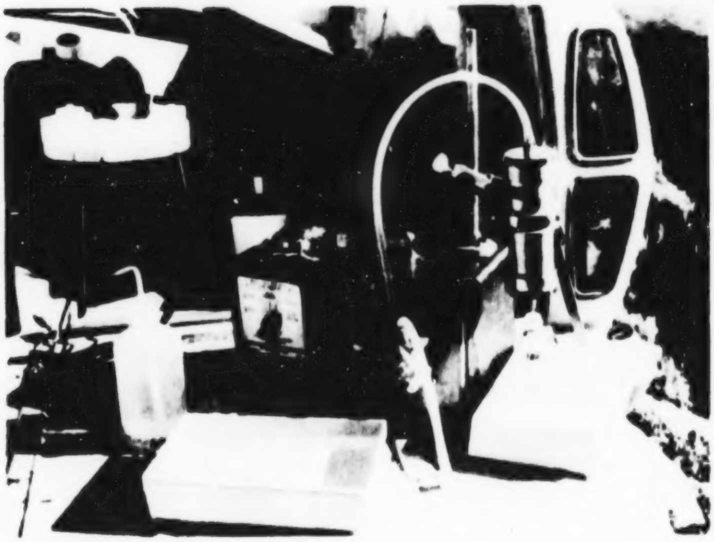

Fig. 6. Organic carbon filtration unit.

SAMPLE PRESERVATION

Samples for major cation, iron, and arsenic analysis are acidified with 2 ml hydrochloric acid/250 ml; samples for mercury analysis are treated with 10 ml 5% potassium permanganate/400 ml (Avotins and Jenne, 1975); trace element samples are acidified with 5 ml redistilled nitric acid/l. The pH of acidified samples is checked at the end of the day to assure that a pH of <1.2 has been reached. The above three preservatives are transported to the field in standard borosilicate glass ampules, avoiding the risk of contamination, total loss or injury associated with single-container storage. The nitric acid must be stored in an ampule with scored constriction, as the color-break ring of the standard ampules contains some trace elements, notably lead, which will contaminate a trace-element sample.

Sulfide samples are fixed by sequentially adding 2 ml of 1 M zinc acetate and 2 ml of 1 M sodium hydroxide/250 ml (Amer. Public Hlth. Assoc., 1970). Since the former solution contains a large amount of zinc, a frequently determined metal, it is stored in a septum-stoppered bottle and dispensed with a disposable syringe, both of which are stored in a zip-lock bag. Sulfide and dissolved organic carbon samples are chilled as soon as possible after collection, and held at 4°C until analysis. Aliquots for silica analyses are normally diluted 10-fold at the end of the day of collection, but samples containing >700 mg/l silica must be diluted immediately (M. Thompson, oral comm., 1976). Nutrient samples are frozen as soon as possible with dry ice, and kept frozen until analysis.

GAS COLLECTION

Geothermal gases (other than steam) generally consist of carbon dioxide with lesser quantities of nitrogen, methane, hydrogen sulfide, hydrogen, oxygen, C_2-C_6 hydrocarbons, and inert gases in approximate order of decreasing abundance.

Two methods of geothermal gas collection have been tested. One method, described in more detail elsewhere (Truesdell and Pering, 1974), utilizes syringes for both volume measurement and gas absorption in sodium hydroxide, and is particularly suited for partial field analysis. The other method, in which absorption in sodium hydroxide takes place in an evacuated bottle, is suited for isotope analysis wherein larger quantities of gas are required. In the syringe method, hydrogen sulfide is fixed by absorption in sodium hydroxide solution followed by immediate precipitation using cadmium acetate or by eventual total oxidation to sulfate. The sodium hydroxide also absorbs carbon dioxide, greatly reducing the bulk of the gas sample, and the reduction in volume of gas accurately indicates the ratio of carbon dioxide plus hydrogen sulfide to other gases. If cadmium sulfide is precipitated, the intensity of the yellow color gives a rough indication of the relative quantity of hydrogen sulfide.

The syringe apparatus (Fig. 7) is flushed with spring water and 10 to 20 ml of 3 M sodium hydroxide solution is introduced into syringe B. Gas is drawn into syringe A, its volume measured by noting the change of position of the plunger and it is pumped into syringe B.

With vigorous shaking of this syringe, carbon dioxide and hydrogen sulfide are absorbed and the decrease in volume gives a field analysis for these gases which has been found to be within ± 1% of the amount found absorbed in the sodium hydroxide. When 25 ml of residual gas have accumulated, these are transferred into the evacuated gas bottle. The procedure is repeated until the gas bottle is full. Detailed descriptions of the construction of the apparatus and of its manipulation during sampling are given by Truesdell and Pering (1974). After sample collection, half of the sodium hydroxide solution is saved for carbon dioxide analysis and half is treated with cadmium acetate to preserve hydrogen sulfide.

The second method used for gas collection is similar in principle. 50 ml of sodium hydroxide solution is contained in an evacuated gas bottle. When the tubing and funnel are flushed with water and filled with gas, the bottle is attached and opened so that the gas bubbles through the caustic solution. The carbon dioxide and hydrogen sulfide are absorbed rapidly during shaking. The collection is complete when no more gas is absorbed in a reasonable time. This method is a simplification of that proposed by Giggenbach (1976) for volcanic gases.

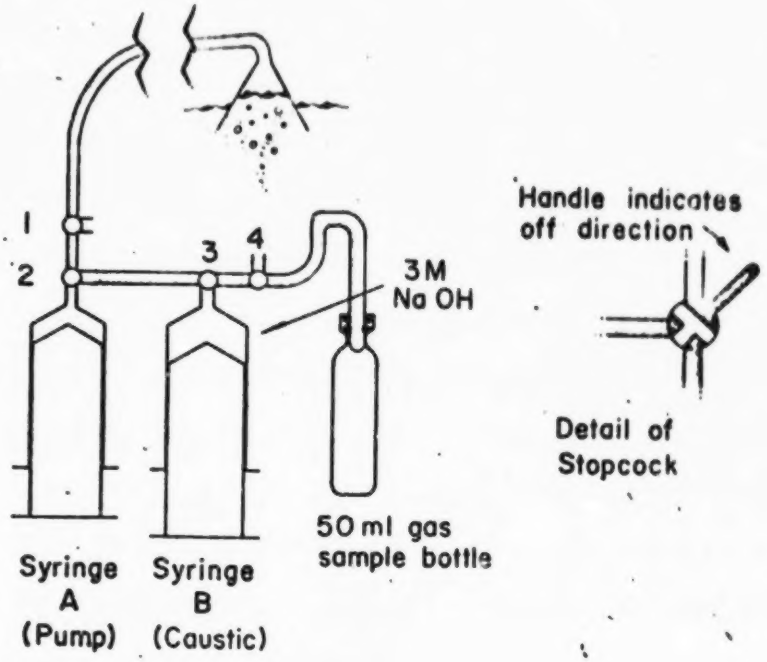
Handle indicates
off direction
1
2
3
4
3M
Na OH
Detail of
Stopcock
50 ml gas
sample bottle
Syringe
A
(Pump)
Syringe
B
(Caustic)

Fig. 7. Syringe apparatus for gas collection.

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